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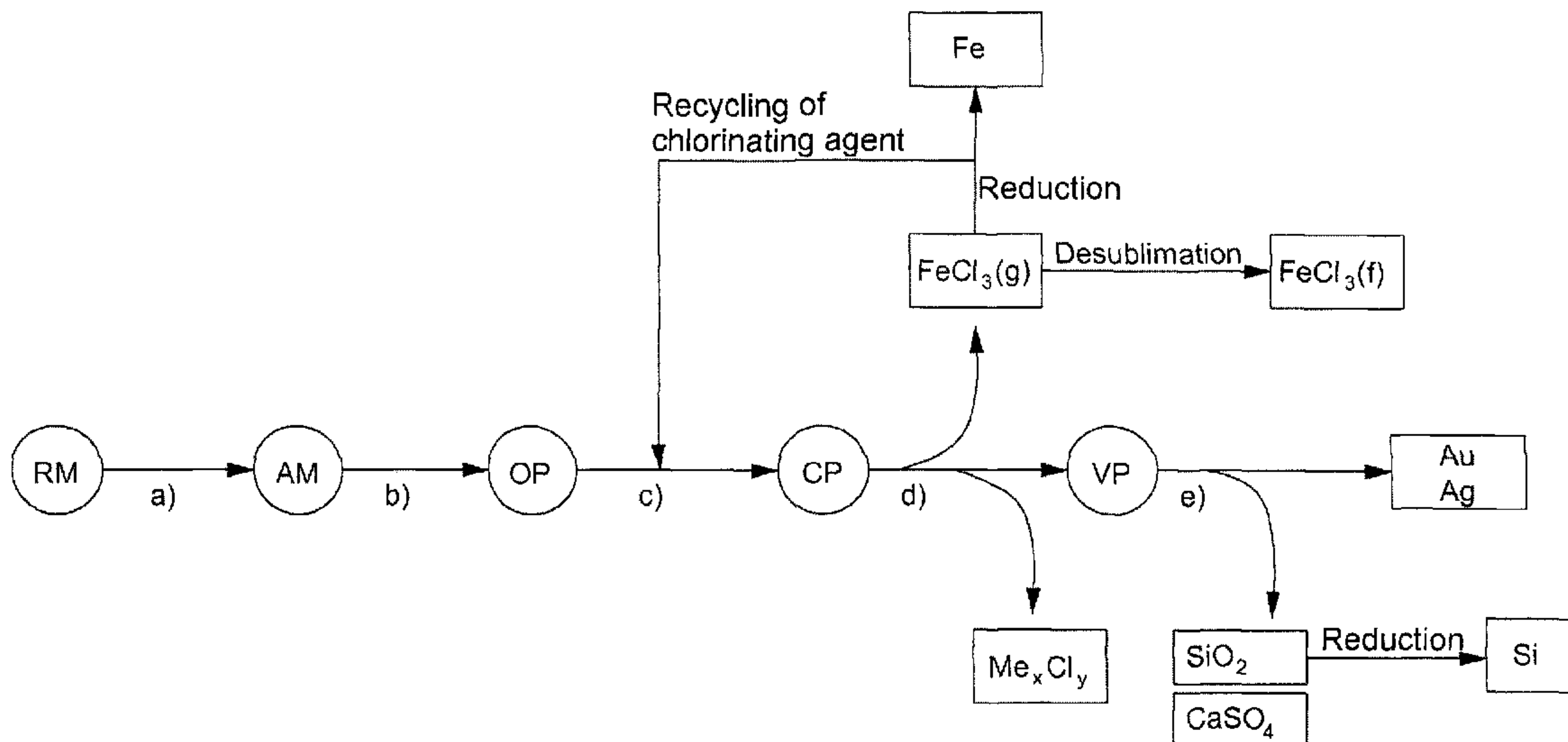
(72) **Inventeurs/Inventors:**
BOHRINGER, BERTRAM, DE;
SCHONFELD, RAIK, DE;
DYACHENKO, ALEXANDER, DE;
LARIN, VALERIY, DE

(73) **Propriétaire/Owner:**
BLUCHER GMBH, DE

(74) **Agent:** GOWLING WLG (CANADA) LLP

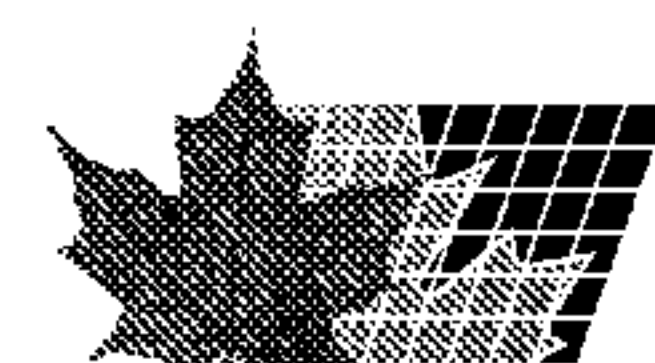
(54) **Titre : PROCÉDE ET INSTALLATION POUR LA PRODUCTION DE FER A PARTIR DE CENDRES DE PYRITE**

(54) **Title: METHOD AND PLANT FOR PRODUCING IRON FROM ROASTED PYRITES**



(57) **Abrégé/Abstract:**

The invention relates to a method and a recovery system for obtaining/recovering metallic iron and/or iron compounds, in particular iron chloride, from ores and/or ore tailings, especially from pyrite tailings, preferably from roasted pyrites produced during sulphuric acid manufacture.



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(71) Anmelder: BLÜCHER GMBH [DE/DE]; Mettmanner
Strasse 25, 40699 Erkrath (DE).

(72) Erfinder: BÖHRINGER, Bertram; c/o Blücher GmbH,
Mettmanner Strasse 25, 40699 Erkrath (DE).
SCHÖNFELD, Raik; c/o Blücher GmbH, Mettmanner
Strasse 25, 40699 Erkrath (DE). DYACHENKO,
Alexander; c/o Blücher GmbH, Mettmanner Strasse 25,
40699 Erkrath (DE). LARIN, Valeriy; c/o Blücher GmbH,
Mettmanner Strasse 25, 40699 Erkrath (DE).

(74) Anwalt: STREHLKE, Ingo K.; Von Rohr Patentanwälte
Partnerschaft, Rüttenscheider Strasse 62, 45130 Essen
(DE).

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(54) Title: METHOD AND PLANT FOR PRODUCING IRON FROM ROASTED PYRITES

(54) Bezeichnung : VERFAHREN UND ANLAGE ZUR EISENGEWINNUNG AUS KIESABBRAUD

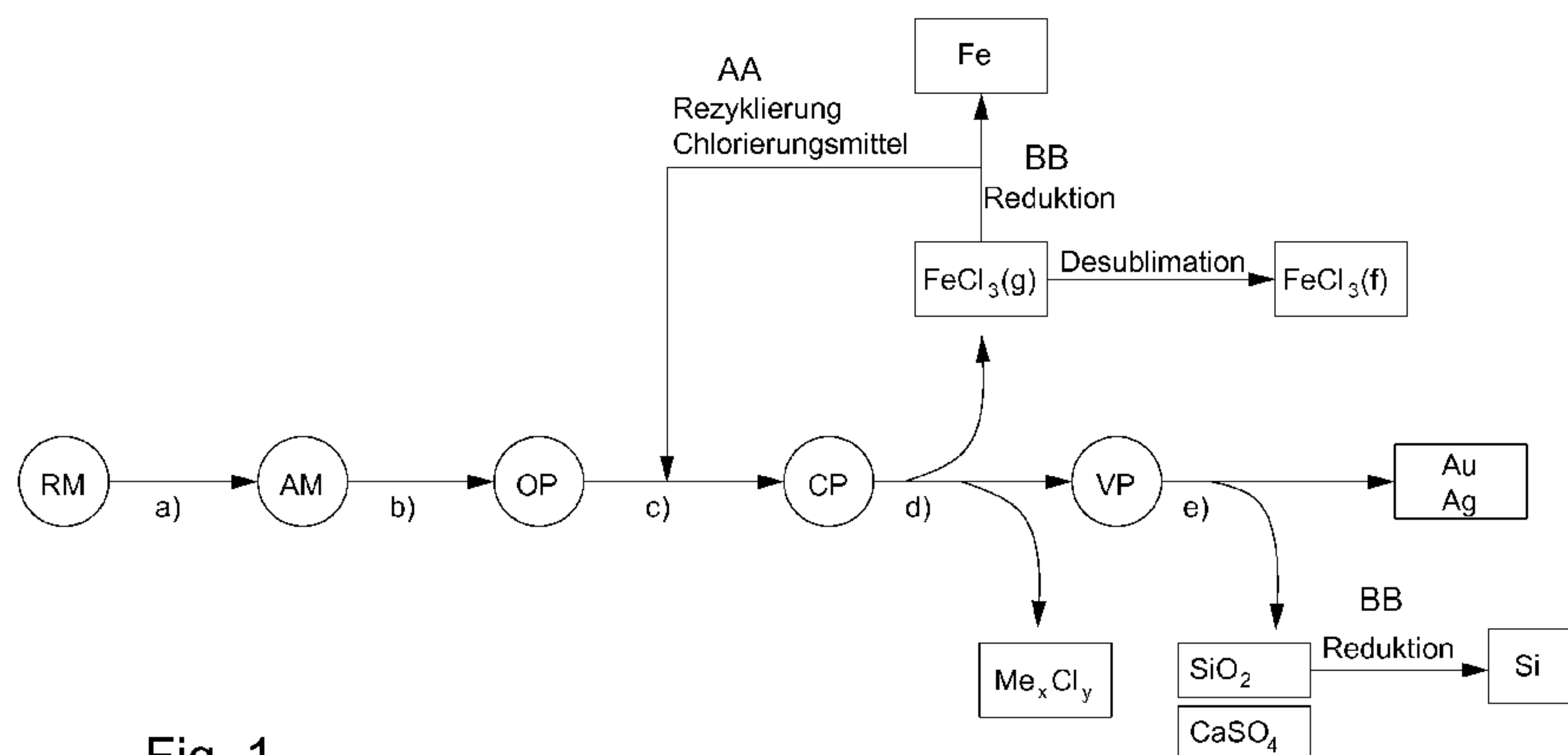


Fig. 1

AA Recycling of chlorinating agent
BB Reduction

(57) Abstract: The invention relates to a method and a recovery system for obtaining/recovering metallic iron and/or iron compounds, in particular iron chloride, from ores and/or ore tailings, especially from pyrite tailings, preferably from roasted pyrites produced during sulphuric acid manufacture.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft ein Verfahren sowie eine Rückgewinnungs-Anlage zur (Rück-)Gewinnung von metallischem Eisen und/oder Eisenverbindungen, insbesondere Eisenchlorid, aus Erzen und/oder Erzrückständen, vorzugsweise aus Pyritrückständen, besonders bevorzugt aus bei der Schwefelsäureherstellung anfallendem Kiesabbrand.



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**Method and plant for producing iron from roasted
pyrites**

The present invention relates to the technical field of
5 the extraction of metals, more particularly of iron,
and/or of non-noble nonferrous metals and/or noble
metals from ores and/or ore residues, preferably from
pyrite residues or pyrite cinder, more particularly
roasted pyrites.

10

The present invention relates more particularly to a
method for obtaining/recovering metallic iron or iron
compounds, more particularly iron chloride, from ores
and/or ore residues, preferably from pyrite residues,
15 more preferably from roasted pyrites obtained in the
production of sulfuric acid.

Furthermore, the present invention relates to a
corresponding recovery plant, more particularly for
20 obtaining/recovering metallic iron or iron compounds,
more particularly iron chloride, from ores and/or ore
residues, preferably from pyrite residues, very
preferably from roasted pyrites obtained in the
production of sulfuric acid, it being possible for the
25 plant of the invention to be used to implement the
method of the invention.

The present invention accordingly also relates to the
use of the recovery plant of the invention in the
30 method according to the invention for
obtaining/recovering metallic iron or iron compounds,
more particularly iron chloride, from ores and/or ore
residues.

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In general, ores comprise, in particular, chemical compounds of metals, such as iron compounds, in the form of iron oxides, iron carbonates and iron sulfides, for example, it being possible for the metal compounds
5 in question to be present in the ore as a mixture with nonferrous minerals.

The most important iron ores include magnetite, limonite, hematite and siderite. While iron in the case
10 of magnetite is in the form of iron(II, III) oxide (Fe_3O_4), iron in hematite is encountered fundamentally as iron(II) oxide (Fe_2O_3). In siderite, furthermore, iron is primarily in the form of iron(II) carbonate (FeCO_3).

15

Known additionally, however, are natural ores in which iron is present primarily in conjunction with sulfur. These include, in particular, pyrite, which on account of its metallic luster and its brassy yellow coloring
20 is also known synonymously as fool's gold.

In particular, pyrite includes a series of further technologically and/or economically significant metal components, such as zinc, copper, cobalt and lead, for
25 example, and also further ingredients based on calcium and silicon, which in general, as a result of the primary industrial utilization of pyrite for the purpose of producing sulfuric acid, are not valorized and hence remain, so to speak, unutilized in the
30 material or resulting roasted pyrites.

As mentioned above, iron in pyrite is present in particular in the form of the sulfide, more

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particularly as iron(II) disulfide or FeS_2 ; in this context, pyrite represents the most widespread sulfide mineral. On an industrial scale, it is used as starting material for producing or obtaining sulfuric acid, with
5 the resulting residues being referred to as pyrite cinder or, synonymously, as purple ore or roasted pyrites.

In the course of the production of sulfuric acid using
10 pyrite as starting material, the general procedure in the prior art is to subject pyrite, as sulfidic metal ore, to roasting in the presence of atmospheric oxygen, with iron sulfide present in pyrite giving rise first of all to sulfur dioxide (SO_2) and to iron oxides in
15 different oxidation states. Subsequently, particularly as part of what is called a contact method or in a contact kiln, the resulting sulfur dioxide is oxidized using a catalyst, vanadium pentoxide, for example, and in the presence of additional oxygen, to form sulfur
20 trioxide (SO_3). Subsequent adsorption and/or reaction with water then produces sulfuric acid (H_2SO_4).

In summary, therefore, the production of sulfuric acid starting from pyrite is carried out in particular in
25 the form of a four-stage operation, the method comprising the following steps:

- (i) roasting of pyrite, for example in a fluidized
bed roasting furnace, for obtaining sulfur
30 dioxide starting from iron sulfide or iron disulfide or iron(II) disulfide (with the corresponding chemical reaction equation
 $4 \text{FeS}_2 + 11 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 + 8 \text{SO}_2$);

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- (ii) subsequent gas purification, particularly for purifying sulfur dioxide obtained beforehand;
- 5 (iii) oxidation of sulfur dioxide to sulfur trioxide (with the corresponding chemical reaction equation $2 \text{SO}_2 + \text{O}_2 \rightarrow 2 \text{SO}_3$), a reaction which can be carried out with the use of catalyst in a contact reactor or tray reactor; and
- 10 (iv) adsorption of sulfur trioxide with hydrous sulfuric acid, more particularly concentrated hydrous sulfuric acid, for the purpose of obtaining further sulfuric acid, with the sulfur
- 15 trioxide acting as an anhydride of the resulting sulfuric acid (with the chemical reaction equation $\text{SO}_3 + \text{H}_2\text{SO}_4(\text{H}_2\text{O}) \rightarrow 2 \text{H}_2\text{SO}_4$).

Generally speaking, on the industrial scale, sulfuric

20 acid is employed in very large quantities and in numerous sectors of the chemical industry: a large proportion of the sulfuric acid produced goes into the production of fertilizers. Furthermore, sulfuric acid acts as a starting product or intermediate in the

25 production of other industrially relevant products, such as catalysts, surfactants, acids, such as hydrofluoric acid, sulfates, drying agents, reaction auxiliaries, and the like. Not least on account of the numerous possible uses of sulfuric acid, it is clear

30 that there is a high demand for it: accordingly, worldwide production of sulfuric acid has exceeded the order of magnitude of 200 million metric tonnes per annum, making sulfuric acid globally the most produced

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chemical.

Against this background as well it is clear that in the production of sulfuric acid using pyrite as starting material, large quantities of pyrite cinder or roasted pyrites result. These, generally speaking, are the waste or residue arising in the form of pyrite from the roasting of the starting materials and starting ores employed. Roasted pyrites, in particular, comprise a solid residue arising in the production of sulfur dioxide or sulfuric acid by thermal treatment of pyrite. The general assumption is that on a worldwide basis, at least 20 million metric tonnes of roasted pyrites are obtained annually in connection with the production of sulfuric acid.

The roasted pyrites are generally stored or land filled at the site of production, there already being very large stocks of roasted pyrites present on a worldwide basis in connection with the production of sulfuric acid, which has been practiced from the end of the 19th Century onward. Since the pyrite forming the basis for the production of sulfuric acid, before being processed, is generally comminuted or ground, the resulting roasted pyrites take the form, generally, of a finely particulate and, in particular, relatively homogeneous substance.

As far as the resulting pyrite cinder or roasted pyrites, generally, are concerned, they comprise large amounts of iron and also economically relevant amounts of further metals, including noble metals as well, which are not removed from the starting material in the

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course of sulfuric acid production, meaning that roasted pyrites as such, against this background, are a valuable raw material for the recovery of economically relevant quantities of metals, including noble metals.

5

In particular, roasted pyrites comprise iron oxides in the form of FeO , Fe_2O_3 (hematite) and/or Fe_3O_4 (magnetite), and residual amounts of FeS_2 (iron disulfide), which are responsible in particular for the reddish coloration of roasted pyrites. As well as silicon dioxide (SiO_2) and sulfates, particularly in the form of calcium sulfate (CaSO_4), roasted pyrites also include significant quantities of the metals zinc, copper, cobalt, titanium, manganese, vanadium, chromium and lead. Furthermore, roasted pyrites also comprise noble metals, more particularly in the form of gold and/or silver. In this regard as well, roasted pyrites harbor a not least economically high potential in relation to the extraction or recovery of metals, non-noble nonferrous metals, and noble metals.

In this respect it is also notable that iron, with a weight fraction of 95% in relation to the total metals utilized, is the most widely used metal globally. Iron, for example, constitutes the principal constituent of steel. The reason for the extensive use of iron lies not only in its wide availability but also, in particular, in the fact that iron has outstanding properties in respect of strength and toughness, especially insofar as iron is present in the form of alloys with other metals, such as chromium, molybdenum, and nickel. On account of these properties, iron is a basic material for many sectors of industry. In

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particular, iron in the form of steel is used in producing vehicles, ships, and across the construction sector, as steel-reinforced concrete, for example. A further factor is that iron represents a ferromagnetic metal and, consequently, is also important for large-scale industrial use in the area of electromagnetism, such as in generators, transformers, electrical inductors, relays, and electrical motors. In this context, iron is used either in pure form or in combination, for example, with silicon, aluminum, cobalt or nickel as a soft-magnetic core material for the guiding of magnetic fields and/or for the shielding of magnetic fields, or for increasing the inductivity. Iron is also used in the chemical sector, especially in the form of iron powder. In 2010, worldwide production of crude iron exceeded the figure of 1000 million metric tonnes. This shows that on a worldwide basis there is a very high demand for iron.

Against this background, initial approaches in the prior art have been pursued into making economic use of the roasted pyrites resulting as a waste product of sulfuric acid production.

Thus, for example, the residue in the form of pyrite cinder or roasted pyrites that remains in the getting of sulfuric acid is used in blast furnaces. The focus in this regard is on the obtention of iron, with the underlying methods occasionally not being economically and environmentally optimal, however, and recovery of further substances not being provided.

Furthermore, US 4 259 106 A relates to a method for the

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roasting of an iron-containing starting material, such as roasted pyrites, which also comprises further metals, the intention being to subject the further metals to a chlorination. With regard to the
5 chlorinating reagent, calcium chloride is the authoritative reference point. In this context, chlorination only of non-iron metals is envisaged, the intention being that iron as such should remain in the melt. A disadvantage, moreover, is the high energy
10 consumption associated with the underlying method.

Moreover, GB 1 236 345 A is not aimed at recovery of iron specifically. In particular, the intention is only that there should be chlorination of non-iron metals at
15 the same time as the roasting of the starting material. On the basis of the chlorinating agents used and the process regime selected, moreover, there is a high resulting corrosion activity, which is detrimental particularly to the apparatus on which the method is
20 based.

Furthermore, EP 0 538 168 A1 is not directed to the chlorination and recovery of iron from roasted pyrites. Instead, this document is aimed at optimizing the
25 cyanide leaching indicated for the recovery of gold and silver, there being no intention to recover metallic iron. The process regime selected, moreover, is economically disadvantageous.

30 Furthermore, CN 101 067 163 A describes a treatment method for pyrite where neither roasting nor chlorination is envisaged. For this reason as well, the isolation of individual components from the raw

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material is not very efficient.

Furthermore, CN 102 605 172 A relates to a method involving pyrite roasting, which envisages subsequent
5 reduction of the cinder using a biomass. As a result of the carbon present in the biomass, the aim is to reduce iron(III) oxide to metallic iron. The resulting metallic iron is to be isolated via magnetic separation. Extensive recovery of further metals is not
10 envisaged.

Moreover, CN 102 502 527 A is geared to the use of iron sulfate as a starting substance, which with pyrite and elemental sulfur is to be reacted to give iron powder.
15 Chlorination within the recovery process is not envisaged. Selective separation of different metal components is not effectively ensured.

CN 102 251 067 A is aimed at a treatment of pyrite or
20 pyrite cinder without chlorination, the intention being to remove metallic constituents by means of leaching methods. Disadvantages here, however, are the high level of chemical usage and also the occasionally low selectivity of the separation procedure.

25
CN 102 225 374 A relates to magnetic separation of iron following removal of other metals from pyrite cinder. Chlorination of metallic components is not envisaged. Nor is targeted and selected separation of different
30 metal components envisaged.

Furthermore, CN 102 121 059 A relates to a roasting method for pyrite. Chlorination of metallic components

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is not described. Furthermore, iron is reduced using carbon. A disadvantage in this case, however, is that occasionally the resulting metallic iron is not of high purity, since impurities may result from the carbon
5 used for the reduction.

CN 102 344 124 A describes the conversion of iron sulfate via the monohydrate form into sulfuric acid, iron and iron oxide, with pyrite being used as starting
10 material. There is no description of specific chlorination. Similarly, extensive separation and recovery of different metals is not envisaged.

Moreover, GB 1 350 392 A relates to the obtention of
15 non-noble nonferrous metals from pyrite after roasting and chlorination of the non-noble nonferrous metals. Chlorination of iron is not envisaged. The iron component is to remain in the form of iron oxide in the residue. Accordingly, efficient separation of all the
20 components is not possible.

US 4 576 812 A relates to a method whereby iron chloride is used as a chloride source: starting from iron chloride and employing oxygen, the aim
25 subsequently is to produce iron(III) oxide, which is then used for the recovery of iron. Roasting of the starting material is not described, and so occasionally dispersant starting materials are present.

30 Furthermore, DE 2 005 951 A is directed to a method for processing pyrite cinder to form feedstocks for blast furnaces. The pyrite cinder in this case is to be pelletized and burnt in a rotary furnace in the

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presence of calcium chloride, the purpose of the calcium chloride being to oxidize the iron. No further processing or separation is envisaged, and/or is impossible on account of the specific process regime.

5

DE 637 443 A relates to the reduction of iron chloride using steam and optionally coal, starting from materials containing ferrous sulfide, the aim being to obtain elemental sulfur.

10

The scientific publication *Trumbull R.C. et al., "Transactions of the Institution of Mining and Metallurgy", 58, 1949, pages 1 to 31*, relates to a method for the treatment of pyrite cinder according to the so-called Henderson process. In accordance with this method, the pyrite cinder is first of all comminuted and then subjected to roasting in the presence of sodium chloride. From the residue obtained in this way, non-noble nonferrous metals are removed.

20 There is, however, no intention of recovering iron from the pyrite cinder treated in this way. The roasting takes place in the presence of sodium chloride at temperatures of above 350°C and in the presence of oxygen.

25

The scientific publication *Pitsch H. et al., Revista de Metalurgia, 6, 1970, pages 490 to 500*, relates to a method for removing non-noble nonferrous metals from pyrite cinder using chlorinating reagents in the form of chlorine gas or calcium chloride. There is no intention to recover iron from the treated pyrite cinder. The pyrite cinder is chlorinated in an oxidizing atmosphere at high temperatures at 1000 to

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1200°C, with the consequence that any resultant iron(III) chloride is immediately converted to iron(III) oxide and, consequently, there is no iron(III) chloride present after the chlorination.

5

The processing methods known in the prior art for metallic ores, especially pyrite, or for waste products arising in the processing of these ores, such as roasted pyrites, are therefore often associated with
10 the drawback that on the one hand the underlying methods are technically complex and are carried out using a high volume of chemicals, and secondly that comprehensive separation and/or recovery of different metal components is not possible. Equally, some of the
15 plant used for the methods in question, owing to the complex process regime, is costly and inconvenient.

Against this technical background, therefore, the object addressed by the present invention is that of
20 providing an efficient method and a corresponding plant and device for obtaining or recovering raw material from ores and/or ore residues, and/or for recovering in particular iron or iron compounds, more particularly in the form of iron chloride, and also, optionally,
25 further components, in particular from roasted pyrites arising in the production of sulfuric acid, where the disadvantages outlined above, affecting the prior art, are to be at least largely avoided or else at least attenuated.

30

An object of the present invention is seen in particular as being that of providing an efficient method and relevant plant and/or devices, the aim

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thereof being to permit extremely comprehensive and selective recovery in particular of iron or iron compounds, more particularly iron chloride, from the parent roasted pyrites or residue. In this case, the
5 intention is for the method and the corresponding plants to also permit in addition to this the removal or recovery of a large number of different metals, and also noble metals, from the parent roasted pyrite, selectively and with high purity.

10

Furthermore, a further object of the present invention lies in the provision of a highly efficient method, minimizing the usage of chemicals or of energy, for the recovery of iron, or iron compounds, more particularly
15 iron chloride, from a parent pyrite residue or roasted pyrites, particularly with regard to recycling or re-utilization of the process chemicals used as part of the recovery procedure.

20 Moreover, according to a further objective of the present invention, the aim is to provide corresponding plant or devices which allow an efficient regime for the selective recovery in particular of iron and iron compounds, such as iron chloride, from the pyrite
25 residue or roasted pyrites, where the plants and devices in question are at the same time also to be optimized from an economic and environmental standpoint.

30 The objective outlined above is achieved in accordance with the invention by the subject matter of claim 1, which concerns the method of the invention for obtaining/recovering metallic iron or iron compounds,

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more particularly iron chloride, from ores or ore residues, preferably from pyrite residues, more preferably from roasted pyrites obtained in the production of sulfuric acid; further advantageous
5 embodiments and developments of this aspect of the invention are subject matter of the corresponding co-independent method claim and also of the underlying dependent method claims.

10 Further provided by the present invention is additionally the recovery plant of the invention, preferably for obtaining/recovering metallic iron and/or iron compounds, more particularly iron chloride,
15 residues, very preferably from roasted pyrites obtained in the production of sulfuric acid, as defined in the corresponding independent claim relating to the plant of the invention; further advantageous embodiments and developments of the plant of the invention are subject
20 matter of the corresponding co-independent claim and the dependent claims relating to the plant of the invention.

Moreover, the present invention provides for the use of
25 the recovery plant according to the invention in the method of the invention for obtaining/recovering iron or iron compounds, more particularly iron chloride, from ores and/or ore residues in accordance with the relevant use claim.

30

It will be appreciated that configurations, embodiments, advantages and the like which are cited below in relation only to one aspect of the invention,

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in order to avoid repetition, are of course equally valid in relation to the other aspects of the invention.

5 It will further be appreciated that in the context of values, numbers and ranges specified below, the specified ranges should not be interpreted as imposing any restriction; it is self-evident that, by virtue of the specific case or specific application, deviations
10 may be made from the stated ranges and figures, without departing the scope of the present invention.

It is the case, moreover, that all value and parameter indications given hereinafter, or the like, can
15 fundamentally be ascertained or determined using standardized or explicitly stated determination methods or else with determination methods that are familiar per se to the skilled person.

20 For all of the relative or percentage, especially weight-based, quantity figures stated hereinafter, moreover, it should be borne in mind that in the context of the present invention, these figures should be selected and/or combined in such a way that the
25 total - possibly including further components or ingredients or constituents, especially as defined hereinafter - always results as 100% or 100 wt%. This, however, is self-evident to the skilled person.

30 On this basis, the present invention is described in more detail below.

A subject of the present invention,

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therefore - according to a **first** aspect of the present invention - is a method for obtaining/recovering metallic iron and/or iron compounds, more particularly iron chloride, from ores and/or ore residues, more particularly a method for recovering metals from ores and/or ore residuals, preferably from pyrite residues, more preferably from roasted pyrites obtained in the production of sulfuric acid, where the method comprises the following method steps:

- 10 (a) providing, more particularly processing, of a starting material in the form of at least one ore and/or ore residue, more particularly of at least one pyrite residue, preferably of one or more roasted pyrites obtained in the production of sulfuric acid, where the starting material comprises
- 15 i) iron, preferably as main constituent, and
ii) at least one noble metal, more particularly gold and/or silver, and also
- 20 iii) at least one further metal, preferably selected from the group of copper, zinc, lead, cobalt, titanium, manganese, vanadium and chromium, more preferably selected from the group of copper, zinc, lead and cobalt;
- 25 (b) oxidation treatment, more particularly calcining and/or oxidative roasting, of the starting material provided in method step (a), preferably using at least one oxidizing agent, more particularly oxygen, to give iron oxide and oxides of the further metals;
- 30 (c) chlorination of the oxidation products, more particularly of iron oxide and oxides of the further metals, using at least one chlorinating

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agent, more particularly a recyclable chlorinating agent, comprising the chlorination of iron oxide and oxides of the further metals to give iron chloride, more particularly iron(III) chloride, and chlorides of the further metals;

5 (d) selective removing and/or isolation of iron chloride, more particularly iron(III) chloride, from the product mixture obtained in method step (c), and optional subsequent removing of chlorides

10 of the further metals from the product mixture freed from iron chloride, the selective removing and/or isolation of iron chloride, more particularly iron(III) chloride, taking place by sublimation of the iron chloride, more

15 particularly iron(III) chloride, and the iron chloride, more particularly iron(III) chloride, removed selectively in this way is obtained as such by subsequent desublimation, or the iron chloride, more particularly iron(III) chloride,

20 removed selectively in this way is subjected to reduction to give metallic iron;

where the above-stated method steps (a) to (d) are carried out in the order listed above.

25 The method of the invention therefore relates significantly to the targeted or selective obtaining of raw material of metallic iron and of iron compounds more particularly from pyrite residues and, preferably, from roasted pyrites obtained in the production of

30 sulfuric acid. The method of the invention thus relates to the targeted or selective recovery, more particularly from pyrite residues and, preferably, from roasted pyrites obtained in the production of sulfuric

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acid. A particular focus of the method according to the invention lies in this case on the targeted isolation of iron, which, in accordance with the invention, both, in particular, in the form of iron chloride as an important commercial and industrial product, and in the form of metallic iron as a significant raw material, especially for the metal industry, can be provided. In this case, both metallic iron as such and the corresponding iron compounds (specifically in the form of iron chloride, preferably in the form of iron(III) chloride) can be provided with high purity.

As a result of the selective sublimation of iron chloride, more particularly iron(III) chloride (FeCl_3), from the product mixture it is possible to realize a controlled removing of the iron component from the product mixture, so that on this basis, so to speak, the main component of the starting material used, namely iron, can be isolated or removed, specifically in the form of the corresponding iron chloride. This selective sublimation or removing of iron chloride takes place in particular on the basis of the deliberate selection of the sublimation temperature. The reason is - without wishing to be confined to this theory - that the iron chloride, more preferably iron(III) chloride (FeCl_3), that is to be removed and/or isolated has sublimation properties differing from those of the chlorides of the further metals and/or further components in the product mixture, especially in terms of the fact that iron chloride, particularly in comparison to the other chlorides, has a lower sublimation temperature. Through the specific selection of the sublimation temperature it is

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possible, therefore, to carry out selective removal of the iron component from the product mixture.

In accordance with the invention, the iron chloride
5 obtained or isolated may on the one hand be provided
and, on the other hand, further processing to metallic
iron may be envisaged, by means of reduction. In
particular for this purpose it is possible for
corresponding sub-streams of the sublimed iron chloride
10 to be used in each case for the desublimation and for
the reduction, respectively. Accordingly, in method
step (d), a particular possible procedure is for the
iron chloride, more particularly iron(III) chloride,
removed selectively beforehand by sublimation to be
15 obtained as such at least partly by means of subsequent
desublimation and for the iron chloride, more
particularly iron(III) chloride, removed selectively in
this way to be subjected at least partly to a reduction
to give metallic iron, more particularly with prior
20 division of the sublimed iron chloride into two sub-
streams.

With regard to the iron chloride, more particularly
iron(III) chloride (FeCl_3), removed from the product
25 mixture and, in particular, sublimed, this chloride may
thus be recovered as such: for this purpose, the
removed and/or isolated and in particular sublimed iron
chloride, more particularly iron(III) chloride (FeCl_3),
may be desublimed to give, in particular, solid and/or
30 purified iron chloride, more particularly iron(III)
chloride (FeCl_3). The desublimation may be carried out
in a corresponding desublimation or condensation
device. In this context, in particular, gaseous iron

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chloride may be transferred from the sublimation device into the desublimation device. In this way, in particular, particulate or solid iron chloride is obtained, which as such constitutes an economically relevant industrial or commercial product, particularly with regard to its use as a pigment and/or flocculate and/or precipitant, especially in wastewater treatment plants or the like.

Furthermore, the removed and/or isolated and more particularly sublimed and therefore gaseous iron chloride, more particularly iron(III) chloride (FeCl_3), may be reduced to give metallic iron. In this context it is possible to use at least one reducing agent. The reducing agent is preferably hydrogen or natural gas (especially methane), more preferably hydrogen.

Furthermore, the removing of the iron component, which generally represents a main constituent or a main component of the pyrite cinder or roast pyrites employed in accordance with the invention, takes place in particular, in the sequence of the method to logical procedure, before the optionally provided removing or recovery of the other components. Accordingly, the main component is removed at a very early stage, which firstly leads to high yields in respect of iron as such but also with regard to the removing of further components. This is because, on the basis of the method routine of the invention, as a result of the removing of iron, the relative proportions of the other components in the product mixture freed of iron are increased accordingly, thereby providing optimization, in turn, of recovery of these raw materials, downstream

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of or subsequent to the recovery of iron, especially with regard to reduced deployment of chemicals and/or energy for the purpose of removing the further, non-iron metal components and/or the noble metals. This approach in accordance with the invention thus raises the overall efficiency of the recovery of the further metal components and/or noble metals.

The roasted pyrites used according to the invention are in particular roasted pyrites which originate from the production of sulfuric acid. Roasted pyrites are obtained, in particular, as waste or residue as part of sulfuric acid production. This method of the invention is associated with the central advantage that a large number of raw materials, on the basis of metals and/or metal compounds, can be obtained or isolated from the underlying starting material - which is present as waste material in large quantities; in this context, the method of the invention equally permits a high selectivity in relation to the metal components to be obtained from the starting material. In particular, the method of the invention also permits effective recovery or purification of noble metals, such as gold or silver, that are present in the starting material. Overall, the invention thus provides extensive utilization of the starting material with high selectivity of the material removal.

By virtue of the specific procedure according to the present invention, moreover, at least substantially complete digestion of the starting material is possible, with the possibility being provided equally of the provision of high-purity end products from the

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starting material, thereby ensuring overall, in relation to the purified metal components, high qualities and purities as well.

5 A further central idea in the present invention can be seen, moreover, in the fact that the chlorinating agent used for the chlorination of the metal components, which according to one inventively particularly preferred embodiment, as outlined below, is ammonium
10 chloride (NH_4Cl), can be recycled or regenerated. It should also be emphasized in this context that the starting materials or components used for the recycling are equally obtained themselves or are provided as part of the method of the invention or processing sequence,
15 and so in this way there is a further optimization, particularly since there is no need for the additional use of chemicals for the recycling.

With regard to "recycling" as it is used in the context
20 of the present invention in relation to the chlorinating agent, this term should be understood very broadly. In particular, the term "recycling" pertains to renewed obtention of chlorinating agent used beforehand for the chlorination of the metal components
25 as part of the method of the invention, and exhausted or degraded. The recycling in this case takes place in particular on the basis of chemical reactions, whereby in particular, degradation products originating from the chlorinating agent in the chlorinating process are
30 isolated and used as starting material in subsequent chemical reactions with a corresponding co-reactant for the renewed obtention of the chlorinating agent as a recycle. As set out in detail below, the chlorinating

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agent used in accordance with the invention is, in particular, ammonium chloride (NH_4Cl), and the degradation product obtained as part of the chlorination procedure, namely ammonia (NH_3), is
5 reacted preferentially with an inorganic chlorine compound, more particularly hydrogen chloride, thereby producing the recyclate, namely ammonium chloride, which can in turn be used again as a chlorinating agent.

10

A further advantage of the method of the invention is to be seen in the fact that, as mentioned above, the starting substances needed for the recycling, particularly as part of the method of the invention,
15 are themselves generated or obtained, meaning that in relation to the chlorinating agent it is possible, so to speak, for a closed circuit to result, especially as regards the chlorine constituent, hand in hand with an increased efficiency of the method of the invention,
20 with simultaneously reduced costs and improved environmental balance. In the context of the present invention, however, it is equally possible for the starting materials for the recycling of the chlorinating agent, especially with regard to the
25 inorganic chlorine compound, to be added externally. Against this background as well, the method of the invention features high flexibility, and so the method of the invention, so to speak, can be individually adapted or tailored to some extent against the
30 background of the specific process carried out, as defined below, including in relation to the recycling of the chlorinating agent.

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The procedure according to the invention results in a method which is optimized just as much economically as it is environmentally, with reduced production of waste materials and waste gases, the required deployment of energy for the implementation of the method being reduced at the same time.

In summary, therefore, the present invention for the first time provides a method for the targeted or selective processing particularly of pyrite residues, such as roasted pyrites, that allows an efficient and comprehensive utilization of the waste material or residue - in particular, roasted pyrites originating from sulfuric acid production. It is also important in this regard that the pyrite residues or roasted pyrites in question are available in large quantities for use as a result of the decades-long production of sulfuric acid, meaning that in accordance with the invention it is possible to have recourse to resources that are of corresponding extensiveness. In this context, a further advantage of the approach according to the invention is that from environmentally specific aspects as well, occasionally not unproblematic stockpiles of the aforesaid pyrite residues or roasted pyrites can be consumed or reduced.

As mentioned above, the starting material used in the method of the invention contains a multiplicity of metals and metal components, with iron generally constituting a main constituent. With regard to the parent iron and also the other metallic components, such as copper, zinc, lead, cobalt, titanium, manganese, vanadium and chromium, they are present in

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particular not in metallic form as such, in the starting material used for the method of the invention, but instead in the form of corresponding metal-containing compounds, more particularly in the form of oxides, and in this respect as well the respective metals may be present in different oxidation states. Accordingly, for iron, in relation to the starting material, the case is typically that iron may be present, for example, as iron(II) oxide, iron(II, III) oxide and/or iron(III) oxide, particularly as indicated further below. Furthermore, for the noble metals present in the starting material, preferably in relation to gold, it is the case that the respective noble metals, preferably gold, are present in metallic form in the starting material. With regard to the silver present in the starting material, it may generally be present in the starting material in the form of a compound, more particularly as oxide, but also in metallic form.

20

In the context of the present invention it has proven particularly advantageous if in method step (c) the chlorination is carried out using ammonium chloride as chlorinating agent. In particular, therefore, ammonium chloride (NH₄Cl) ought to be used as chlorinating agent in method step (c). In this context, provision may be made in particular for the ammonium chloride (NH₄Cl) to be used as especially particulate solid and/or as pure substance. The inventively preferably envisaged use of a specific chlorinating agent in the form of ammonium chloride is associated in particular with the advantage that ammonium chloride is outstandingly suitable for recycling and, furthermore, has good applications

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properties, not least in respect of its relatively low toxicity and its presence as a solid, which improves meterability.

- 5 In accordance with the invention, the chlorinating agent, more particularly ammonium chloride, may be supplied to the chlorinating device or introduced into the chlorinating device for the purposes of the chlorination of the oxidation products and/or of
10 aforementioned metals.

In particular in relation to the use of a specific chlorinating agent in the form of ammonium chloride, the conditions within the method of the invention may
15 be such that in method step (c), in the chlorination, especially gaseous ammonia (NH_3) and, optionally, especially gaseous water, preferably especially gaseous ammonia (NH_3), results or result. In this context, in particular, gaseous ammonia (NH_3) may result as a
20 reaction product originating from the chlorination from the chlorinating agent, more particularly ammonium chloride (NH_4Cl). In this regard, reference may be made in particular to the reaction equation (iii) below.

- 25 In accordance with the invention, provision may be made in particular for the chlorinating agent used in method step (c), more particularly ammonium chloride (NH_4Cl), to be recycled by recovery and/or removal of reaction products resulting from the chlorinating agent in the
30 chlorination of the aforementioned metals and/or oxidation products, more particularly of preferably gaseous ammonia (NH_3), and by subsequent reaction of the reaction products, more particularly of preferably

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gaseous ammonia (NH_3), with a preferably inorganic chlorine compound, more particularly hydrogen chloride (HCl).

- 5 In particular, the recycling of the chlorinating agent, more particularly ammonium chloride (NH_4Cl), may be carried out in a reaction or condensation device.

10 In this context, in accordance with the invention, the procedure, for example, may be such that ammonia (NH_3) resulting in the chlorination of the metals and/or oxidation products is taken off from the chlorinating device and introduced into a reaction or condensation device, where it is reacted with the inorganic chlorine
15 compound likewise introduced into the reaction or condensation device, more particularly hydrogen chloride (HCl), in order to give ammonium chloride (NH_4Cl). In this way, the chlorinating agent, more particularly in the form of ammonium chloride (NH_4Cl),
20 can be recycled and supplied again to the chlorinating operation. On the basis of this inventive procedure, therefore, a further method optimization is ensured in the context of the present invention.

- 25 With regard to the reaction or conversion of ammonia (NH_3), on the one hand, and of the inorganic chlorine compound, more particularly hydrogen chloride (HCl), on the other, this reaction or conversion underlying recycling of the chlorinating agent, the reaction or
30 conversion may take place in particular in the gas phase, in particular with resulting ammonium chloride (NH_4) resulting or condensing in solid phase. On the basis of this specific inventive procedure therefore,

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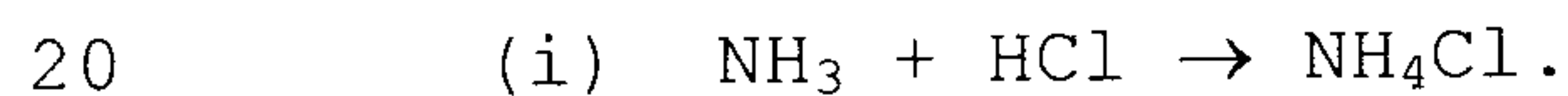
especially particulate ammonium chloride is obtained as a solid in high purity, this being associated with corresponding advantages in the context of the subsequent chlorination.

5

In particular, therefore, provision may be made in the present invention for the reaction products resulting from the chlorinating agent, more particularly ammonia (NH₃) on the one hand and the preferably inorganic chlorine compound, more particularly hydrogen chloride (HCl) on the other, to be reacted in the gas phase, in particular to give ammonium chloride (NH₄Cl), preferably as an especially particulate solid and/or as pure substance.

15

The underlying reaction for the recycling of ammonium chloride may take place in particular according to the following reaction equation (i):



In accordance with the invention, provision may further be made for the resulting or recycled chlorinating agent, more particularly ammonium chloride (NH₄Cl), to be used again in method step (c), more particularly by renewed supply or renewed introduction into the chlorinating device. In particular the resulting or recycled chlorinating agent, more particularly ammonium chloride (NH₄Cl), may be supplied again to the oxidation products for chlorination and/or to the product mixture resulting from method step (b), in method step (c).

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The preferably inorganic chlorine compound, more particularly hydrogen chloride (HCl), can be obtained, according to one particular embodiment of the present invention, by the reduction of iron chloride carried
5 out optionally in method step (d), more particularly with use of a reducing agent, preferably hydrogen or natural gas (more particularly methane), preferably hydrogen. For example, the preferably inorganic chlorine compound, more particularly hydrogen chloride
10 (HCl), may be obtained by reduction of iron chloride.

In this context, in accordance with the invention provision may be made in particular, in relation to the recycling of the chlorinating agent, for the preferably
15 inorganic chlorine compound, more particularly hydrogen chloride (HCl), to be obtained by the optionally provided reduction of iron chloride, preferably iron(III) chloride (FeCl₃), obtained in method step c), more particularly with use of a reducing agent,
20 preferably hydrogen or natural gas (especially methane), more preferably hydrogen.

Equally, the inorganic chlorine compound, more particularly hydrogen chloride (HCl), that is used for
25 the recycling may also be obtained from the optional reduction of the chlorides of the further metals obtained in method step (c), more particularly as defined above.

30 In view of the concept according to the invention, with the specific recycling of the chlorinating agent, the respective substances or reactants can be provided within the method of the invention itself, meaning that

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there is so to speak a closed circuit in terms of the chlorinating agent, this going hand in hand with a reduced level of chemicals used and hence also, in particular, with an improved environmental and economic
5 balance on the part of the method of the invention.

In method step (d) the reduction of the removed and more particularly sublimed iron chloride, more particularly iron(III) chloride, should be carried out
10 using at least one reducing agent. The reducing agent used is very preferably hydrogen. Especially where hydrogen is used as reducing agent, the reduction described above may result not only in metallic iron but also in hydrogen chloride (HCl).

15

In this context there may equally be provision for, as indicated above, the hydrogen chloride (HCl) resulting in the reduction to be used for the recycling of the chlorinating agent, preferably ammonium chloride
20 (NH₄Cl), especially as defined above. In this context there may equally be provision for the especially gaseous ammonia (NH₃), on the one hand, and the hydrogen chloride (HCl), on the other, resulting in the chlorination in method step (c), to be combined and/or
25 brought into contact and reacted to give the recycled chlorinating agent, preferably ammonium chloride (NH₄Cl). In particular it is possible in this context, as described above, to carry out the procedure in a reaction or condensation device. In this context there
30 may in particular be provision, in accordance with the invention, for the gaseous ammonia (NH₃) from the chlorinating device, on the one hand, and the hydrogen chloride (HCl) on the other hand, to be taken off in

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each case from the reduction device and introduced in each case into the reaction or condensation device, and reacted to give ammonium chloride (NH_4Cl).

5 The metallic iron obtained in accordance with the invention is notable for a high purity. Hence in accordance with the invention it may be the case that the metallic iron obtained has a purity of at least 90 wt%, more particularly at least 95 wt%, preferably
10 at least 98 wt%, more preferably at least 99 wt%, very preferably at least 99.5 wt%, especially preferably at least 99.99 wt%, calculated as element and based on the metallic iron obtained.

15 The high purity of the resulting metallic iron is accompanied by corresponding positive properties of the iron, especially in respect of a high magnetic saturation, high electrical conductivity and good acid resistance. The high-purity metallic iron obtained on
20 the basis of the method of the invention, as a commercial product, also corresponds in particular to the quality requirements or quality features of so-called carbonyl iron or ARMCO iron.

25 Not least on the basis of the high proportion of iron in the starting material indicated above, it is possible in accordance with the invention to realize overall high yields in conjunction with high product quality of the metallic iron obtained.

30

In view of the inventive method regime with the controlled oxidation, chlorination and selective sublimation, the iron component can be isolated

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effectively from the parent starting material, resulting in high product yields. In this context, the product mixture obtained in method step (d) and freed from iron chloride, preferably iron(III) chloride
5 (FeCl₃), can have a (residual) iron content of less than 10 wt%, more particularly less than 5 wt%, preferably less than 3 wt%, calculated as element and based on the dry weight of the product mixture. Correspondingly, therefore, in relation to the product
10 mixture obtained in method step (d) and freed from iron, there is a rise in the relative proportion of the other components, and so these components are, so to speak, concentrated in relation to the resulting product mixture, thereby also further improving their
15 subsequent removing or purification and also leading in this respect to higher yields.

In accordance with this aspect of the present invention, the present invention thus relates equally
20 to a method for obtaining/recovering metallic iron and/or iron compounds, more particularly iron chloride, from ores and/or ore residues, preferably from pyrite residues, more preferably from roasted pyrites obtained in the production of sulfuric acid, more particularly
25 as defined in one of the preceding claims, where the method comprises the following method steps:

(a) providing, more particularly processing, of a starting material in the form of at least one ore and/or ore residue, more particularly of at least
30 one pyrite residue, preferably of one or more roasted pyrites obtained in the production of sulfuric acid, where the starting material comprises

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- i) iron, preferably as main constituent, and
ii) at least one noble metal, more particularly
gold and/or silver, and also
iii) at least one further metal, preferably
5 selected from the group of copper, zinc, lead,
cobalt, titanium, manganese, vanadium and
chromium, more preferably selected from the
group of copper, zinc, lead and cobalt
- (b) oxidation treatment, more particularly calcining
10 and/or oxidative roasting, of the starting
material provided in method step (a), preferably
using at least one oxidizing agent, more
particularly oxygen, to give iron oxide and oxides
of the further metals;
- 15 (c) chlorination of the oxidation products, more
particularly of iron oxide and oxides of the
further metals, obtained in method step (b), using
at least one chlorinating agent, more particularly
a recyclable chlorinating agent, comprising the
20 chlorination of iron oxide and oxides of the
further metals, to give iron chloride, more
particularly iron(III) chloride, and chlorides of
the further metals,

25 where the chlorination is carried out using
ammonium chloride as chlorinating agent,

where the chlorinating agent, more particularly
ammonium chloride (NH_4Cl), is recycled by recovery
and/or removing of reaction products resulting
30 from the chlorinating agent in the chlorination of
the oxidation products, more particularly of
preferably gaseous ammonia (NH_3), and subsequent
reaction of the reaction products, more

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particularly of preferably gaseous ammonia (NH_3),
with a preferably inorganic chlorine compound,
more particularly hydrogen chloride (HCl), in
particular where the preferably inorganic chlorine
5 compound, more particularly hydrogen chloride
(HCl), is obtained by the reduction, carried out
optionally in method step (d), of iron chloride,
especially using a reducing agent, preferably
hydrogen or natural gas (especially methane),
10 preferably hydrogen, and

where the chlorinating agent obtained and/or
recycled, more particularly ammonium chloride
(NH_4Cl), is used again in method step (c);

15

(d) selective removing of iron chloride from the
product mixture obtained in method step (c), and
optional subsequent removing of chlorides of the
further metals from the product mixture freed from
20 iron chloride, where the selective removing of
iron chloride, more particularly iron(III)
chloride, takes place by sublimation of the iron
chloride, more particularly iron(III) chloride,
and the iron chloride, more particularly iron(III)
25 chloride, removed selectively in this way is
obtained as such by subsequent desublimation or
the iron chloride, more particularly iron(III)
chloride, removed selectively in this way is
subjected to reduction to give metallic iron;

30

where the above-stated method steps (a) to (d) are
carried out in the order listed above.

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In general as far as the starting material is concerned that is used in the method of the invention, particularly in the form of pyrite residues or roasted pyrites, the starting material may comprise iron in the
5 form of at least one iron oxide. In this context provision may be made in particular for the starting material to comprise iron oxide in the form of iron(II) oxide (FeO), iron(III) oxide (Fe₂O₃) and/or iron(II, III) oxide (Fe₃O₄).

10

In this context the starting material may comprise iron, more particularly in the form of iron oxide, in amounts in the range from 10 wt% to 75 wt%, more particularly in the range from 20 wt% to 70 wt%,
15 preferably in the range from 30 wt% to 65 wt%, more preferably in the range from 40 wt% to 60 wt%, calculated as element and based on the dry weight of the starting material. As noted above, therefore, iron constitutes the main component of the starting material
20 to be processed, and so against this background as well, high recovery quantities or yields in respect of iron are made possible in the context of the method of the invention.

25 Furthermore, the starting material may comprise the noble metal, more particularly gold and/or silver, in amounts in the range from 0.1 g/t to 300 g/t, more particularly in the range from 0.5 g/t to 200 g/t, preferably in the range from 0.75 g/t to 100 g/t, more
30 preferably in the range from 1 g/t to 50 g/t, calculated as element and based on the dry weight of the starting material. The above figures are based on the sum of the stated metals in the starting material.

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The starting material may more particularly comprise gold in the form of metallic gold. Another reason in particular why gold is in metallic form is that on
5 account of the noble physical properties of the element, it is not amenable to combustion in the presence of oxygen.

More particularly, in this context, the starting
10 material may comprise gold in amounts in the range from 0.1 g/t to 15 g/t, more particularly in the range from 0.2 g/t to 10 g/t, preferably in the range from 0.5 g/t to 8 g/t, more preferably in the range from 1 g/t to 5 g/t, calculated as element and based on the dry
15 weight of the starting material.

The starting material may further comprise silver in the form of metallic silver and/or in the form of silver oxide, especially silver(I) oxide. As a noble
20 metal, silver is generally relatively tardy in reactivity, but is less noble than gold, meaning that silver may as indicated above be present in the starting material at least partly in the form of silver oxide, as well.

25

As far as the noble metal silver in the starting material is concerned, moreover, the starting material may comprise silver in amounts in the range from 1 g/t to 300 g/t, more particularly in the range from 2 g/t
30 to 200 g/t, preferably in the range from 3 g/t to 100 g/t, more preferably in the range from 5 g/t to 50 g/t, calculated as element and based on the dry weight of the starting material.

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In view of the presence of noble metals, more particularly gold and/or silver, in relevant amounts, the starting material is also economically significant
5 in relation to the recovery of these noble metals. In particular, on the basis of the method of the invention, in addition to the obtention of iron and other products of economic interest, an efficient and cost-effective method is also provided for the recovery
10 of noble metals, such as gold and/or silver, from the parent starting material, leading to a significant increase in the economics of the method of the invention, since the noble metal components generally have a high material value.

15 Furthermore, the starting material may comprise the further metal, more particularly copper, zinc, lead, cobalt, titanium, manganese, vanadium and/or chromium, preferably copper, zinc, lead and/or cobalt, in amounts
20 in the range from 0.001 wt% to 10 wt%, more particularly in the range from 0.005 wt% to 5 wt%, preferably in the range from 0.0075 wt% to 3 wt%, more preferably in the range from 0.01 wt% to 2 wt%, calculated as element and based on the dry weight of
25 the starting material. The above figures are based on the sum of the stated metals in the starting material.

With regard to the further metal in the form of copper in this context, the starting material may comprise
30 copper in the form of copper oxide, more particularly copper(I) oxide and/or copper(II) oxide.

In this context the starting material may comprise

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copper, more particularly in the form of copper oxide, in amounts in the range from 0.01 wt% to 5 wt%, more particularly in the range from 0.05 wt% to 3 wt%, preferably in the range from 0.075 wt% to 2 wt%, more
5 preferably in the range from 0.1 wt% to 1 wt%, calculated as element and based on the dry weight of the starting material.

With regard, moreover, to the further metal in the form
10 of zinc, the starting material may comprise zinc in the form of zinc oxide, more particularly zinc(II) oxide.

In this context, the starting material may comprise zinc, more particularly in the form of a zinc oxide, in
15 amounts in the range from 0.02 wt% to 10 wt%, more particularly in the range from 0.075 wt% to 5 wt%, preferably in the range from 0.1 wt% to 3 wt%, more preferably in the range from 0.2 wt% to 2 wt%, calculated as element and based on the dry weight of
20 the starting material.

With regard, moreover, to the further metal in the form of lead, the starting material may comprise lead in the form of lead oxide, more particularly lead(II) oxide.

25

In this context, the starting material may comprise lead, more particularly in the form of a lead oxide, in amounts in the range from 0.1 wt% to 5 wt%, more particularly in the range from 0.05 wt% to 4 wt%,
30 preferably in the range from 0.1 wt% to 2 wt%, more preferably in the range from 0.15 wt% to 1.5 wt%, calculated as element and based on the dry weight of the starting material.

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With regard, moreover, to the further metal in the form of cobalt, the starting material may comprise cobalt in the form of cobalt oxide, more particularly cobalt(II) oxide.

In this context, the starting material may comprise cobalt, more particularly in the form of a cobalt oxide, in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%, calculated as element and based on the dry weight of the starting material.

15

With regard, moreover, to the further metal in the form of titanium, the starting material may comprise titanium in the form of titanium oxide.

In this context, the starting material may comprise titanium, more particularly in the form of a titanium oxide, in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%, calculated as element and based on the dry weight of the starting material.

With regard, moreover, to the further metal in the form of manganese, the starting material may comprise manganese in the form of manganese oxide.

In this context, the starting material may comprise

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manganese, more particularly in the form of a manganese oxide, in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%,
5 more preferably in the range from 0.01 wt% to 0.1 wt%, calculated as element and based on the dry weight of the starting material.

With regard, furthermore, to the further metal in the
10 form of vanadium, the starting material may comprise vanadium in the form of vanadium oxide.

In this context, the starting material may comprise vanadium, more particularly in the form of a vanadium
15 oxide, in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%, calculated as element and based on the dry weight of
20 the starting material.

With regard, furthermore, to the further metal in the form of chromium, the starting material may comprise chromium in the form of chromium oxide.

25

In this context, the starting material may comprise chromium, more particularly in the form of a chromium oxide, in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%,
30 preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%, calculated as element and based on the dry weight of the starting material.

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Furthermore, the starting material may comprise at least one semimetal. In particular the semimetal may be selected from the group of silicon, arsenic, selenium, antimony, tellurium and combinations thereof, more particularly silicon. The starting material may comprise the semimetal, more particularly silicon, arsenic, selenium, antimony and/or tellurium, in amounts in the range from 1 wt% to 40 wt%, more particularly in the range from 2 wt% to 30 wt%, preferably in the range from 3 wt% to 20 wt%, more preferably in the range from 4 wt% to 15 wt%, calculated as elements and based on the dry weight of the starting material. The above figures are based on the sum of the semimetals mentioned in the starting material.

Furthermore, the starting material may comprise at least one transition metal, more particularly manganese and/or molybdenum.

In particular, the starting material may comprise silicon, more particularly in the form of silicon oxide, preferably silicon dioxide (SiO_2).

25

More particularly the starting material may comprise silicon, more particularly in the form of silicon oxide, in amounts in the range from 0.5 wt% to 30 wt%, more particularly in the range from 1 wt% to 20 wt%, preferably in the range from 2 wt% to 15 wt%, more preferably in the range from 3 wt% to 10 wt%, calculated as element and based on the dry weight of the starting material.

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Furthermore, the starting material may comprise arsenic, more particularly in amounts of not more than 1 wt%, more particularly not more than 0.5 wt%,
5 preferably not more than 0.3 wt%, calculated as element and based on the dry weight of the starting material.

The starting material may further comprise at least one alkali metal and/or alkaline earth metal, more
10 particularly at least one alkaline earth metal, preferably calcium.

In particular, the alkali metal and/or alkaline earth metal, more particularly the alkaline earth metal,
15 preferably calcium, may be present in the form of at least one salt, more particularly sulfate. The starting material may more particularly comprise calcium sulfate.

20 In this context, the starting material may comprise the alkali metal and/or alkaline earth metal, more particularly the alkaline earth metal, preferably calcium, more preferably in the form of calcium sulfate, in amounts in the range from 0.2 wt% to
25 20 wt%, more particularly in the range from 0.5 wt% to 15 wt%, preferably in the range from 1 wt% to 10 wt%, more preferably in the range from 2 wt% to 8 wt%, calculated as element and based on the dry weight of the starting material.

30

Furthermore, the starting material may comprise at least one nonmetal, more particularly selected from the group of carbon, nitrogen, sulfur and phosphorus, more

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particularly sulfur, preferably in the form of the respective salts.

In this context the starting material may comprise
5 sulfur, more particularly in the form of sulfur-
containing salts, preferably sulfides, such as iron
disulfide, and/or, more preferably, sulfates.

In this context, the starting material may comprise
10 sulfur in amounts in the range from 0.2 wt% to 15 wt%,
more particularly in the range from 0.5 wt% to 10 wt%,
preferably in the range from 1 wt% to 8 wt%, more
preferably in the range from 1.5 wt% to 6 wt%,
calculated as element and based on the dry weight of
15 the starting material.

In accordance with the invention it may in particular
be the case that the starting material, more
particularly the pyrite residue or roasted pyrites,
20 comprises the following ingredients, calculated in each
case as element and based in each case on the dry
weight of the starting material:

- iron, more particularly in the form of iron oxide,
25 for example in amounts in the range from 10 wt% to
75 wt%, more particularly in the range from 20 wt%
to 70 wt%, preferably in the range from 30 wt% to
65 wt%, more preferably in the range from 40 wt%
to 60 wt%;
- 30 - gold, more particularly in amounts in the range
from 0.1 g/t to 15 g/t, more particularly in the
range from 0.2 g/t to 10 g/t, preferably in the
range from 0.5 g/t to 8 g/t, more preferably in

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the range from 1 g/t to 5 g/t;

- silver, more particularly in amounts in the range from 1 g/t to 300 g/t, more particularly in the range from 2 g/t to 200 g/t, preferably in the range from 3 g/t to 100 g/t, more preferably in the range from 5 g/t to 50 g/t;
- copper, more particularly in the form of copper oxide, for example in amounts in the range from 0.01 wt% to 5 wt%, more particularly in the range from 0.05 wt% to 3 wt%, preferably in the range from 0.075 wt% to 2 wt%, more preferably in the range from 0.1 wt% to 1 wt%;
- zinc, more particularly in the form of zinc oxide, for example in amounts in the range from 0.02 wt% to 10 wt%, more particularly in the range from 0.075 wt% to 5 wt%, preferably in the range from 0.1 wt% to 3 wt%, more preferably in the range from 0.2 wt% to 2 wt%;
- lead, more particularly in the form of lead oxide, for example in amounts in the range from 0.01 wt% to 5 wt%, more particularly in the range from 0.05 wt% to 4 wt%, preferably in the range from 0.1 wt% to 2 wt%, more preferably in the range from 0.15 wt% to 1.5 wt%;
- cobalt, more particularly in the form of cobalt oxide, for example in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%;
- titanium, more particularly in the form of titanium oxide, for example in amounts in the range from 0.001 wt% to 2 wt%, more particularly

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- in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%;
- 5 - manganese, more particularly in the form of manganese oxide, for example in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%;
- 10 - vanadium, more particularly in the form of vanadium oxide, for example in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%;
- 15 - chromium, more particularly in the form of chromium oxide, for example in amounts in the range from 0.001 wt% to 2 wt%, more particularly in the range from 0.005 wt% to 1 wt%, preferably in the range from 0.0075 wt% to 0.5 wt%, more preferably in the range from 0.01 wt% to 0.1 wt%;
- 20 - silicon, more particularly in the form of silicon dioxide, for example in amounts in the range from 0.5 wt% to 30 wt%, more particularly in the range from 1 wt% to 20 wt%, preferably in the range from 2 wt% to 15 wt%, more preferably in the range from 3 wt% to 10 wt%;
- 25 - arsenic, for example in amounts of not more than 1 wt%, more particularly not more than 0.5 wt%, preferably not more than 0.3 wt%;
- 30 - calcium, more particularly in the form of calcium sulfate, for example in amounts in the range from 0.2 wt% to 20 wt%, more particularly in the range

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from 0.5 wt% to 15 wt%, preferably in the range from 1 wt% to 10 wt%; and/or

- sulfur, more particularly in the form of sulfur-containing salts for example in amounts in the range from 0.2 wt% to 15 wt%, more particularly in the range from 0.5 wt% to 10 wt%, preferably in the range from 1 wt% to 8 wt%, more preferably in the range from 1.5 wt% to 6 wt%.

10 The starting material here may comprise the following ingredients, based in each case on the dry weight of the starting material:

- iron(II, III) oxide (Fe_3O_4), more particularly in amounts in the range from 10 wt% to 80 wt%, more particularly in the range from 20 wt% to 70 wt%, preferably in the range from 30 wt% to 60 wt%;
- iron(III) oxide (Fe_2O_3), more particularly in amounts in the range from 5 wt% to 50 wt%, more particularly in the range from 10 wt% to 40 wt%, preferably in the range from 15 wt% to 30 wt%;
- silicon dioxide, more particularly in amounts in the range from 2 wt% to 30 wt%, more particularly in the range from 5 wt% to 25 wt%, preferably in the range from 10 wt% to 20 wt%; and/or
- calcium sulfate, more particularly in amounts in the range from 1 wt% to 25 wt%, more particularly in the range from 2 wt% to 20 wt%, preferably in the range from 5 wt% to 15 wt%.

30 The underlying starting material, more particularly in the form of pyrite residues or roasted pyrites, as obtained in particular in the production of sulfuric acid, therefore contains - alongside iron, more

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particularly in the form of iron oxides, as main constituent - numerous further metals or noble metals, meaning that the starting material used in accordance with the invention is outstandingly suitable for use in the context of the present invention, since a multiplicity of different components with industrial and economic relevance, based on metals or noble metals, are recovered or obtained from the starting material, with the method of the invention in this respect enabling selective and comprehensive recovery of the components in question, including in particular in the form of the respective metals.

With regard to the method of the invention as such, provision may be made in accordance with the invention for comminution and/or homogenization of the starting material to be carried out in method step (a), or before implementation of method step (b). In particular the starting material may be adjusted to average particle sizes, more particularly average particle size D_{50} , in the range from 0.1 μm to 10 cm, more particularly 1 μm to 5 cm, preferably 100 μm to 1 cm, more preferably 500 μm to 0.5 cm. For this purpose it is possible to use customary comminuting apparatus well known per se to the skilled person, such as crushing and/or grinding apparatus. The particle size determination may also be carried out with methods well-known per se to the skilled person, based for example on light microscopy, x-ray diffraction, light scattering, such as laser diffractometry. The comminution optionally provided as part of the method of the invention, particularly for obtaining uniform particle sizes in the parent starting material, results

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in better handling and also improved recovery of the respective metal constituents, in particular on the basis of enhanced digestion of the material and the like.

5

Furthermore, provision may be made as part of the present invention for drying of the starting material to be carried out in method step (a) and/or before implementation of method step (b). In this context, the
10 starting material may be heated to temperatures in the range from 50°C to 180°C, more particularly 80°C to 160°C, preferably 100°C to 140°C. It is of advantage in accordance with the invention if the starting material is adjusted to a residual moisture content of not more
15 than 5 wt%, more particularly not more than 3 wt%, preferably not more than 2 wt%, more preferably not more than 1 wt%, based on the dried starting material. The adjustment of the starting material to a defined residual moisture content, as defined above, leads in
20 particular to a further-improved method regime both in terms of the handling of the starting material and in relation to the chemical reaction processes underlying the method of the invention.

25 With further regard to the method of the invention, it is of advantage in accordance with the invention if in method step (b) the oxidation treatment is carried out as solid phase reaction. The oxidation treatment ought in particular to be carried out with heating of the
30 starting material. More particularly the oxidation treatment may be carried out at temperatures in the range from 500°C to 1000°C, more particularly in the range from 600°C to 900°C, preferably in the range from

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650°C to 950°C. In a manner preferred in accordance with the invention, the oxidation treatment ought to be carried out using and/or in the presence of a preferably gaseous oxidizing agent, more particularly
5 air and/or oxygen.

In this context, the oxidation treatment may be carried out in general in the devices suitable for this purpose that are known fundamentally to the skilled person.
10 More particularly the oxidation treatment may be carried out in an oxidation and/or roasting device. In this context, for example, the oxidation and/or roasting device may be selected from the group of rotary kilns, drum kilns, fluidized bed kilns and
15 entrained flow reactors.

In particular, in accordance with the invention, it is provided that, in the oxidation treatment in method step (b), iron is converted at least substantially
20 completely into the trivalent form, more particularly into iron(III), preferably into iron(III) oxide. In particular, in the oxidation treatment in method step (b), therefore, iron(III) is obtained. Moreover, provision may be made in method step (b), in the
25 oxidation treatment, for iron(II, III) oxide and/or iron(II) oxide to be converted into iron(III) oxide.

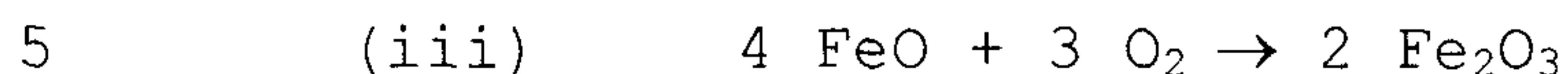
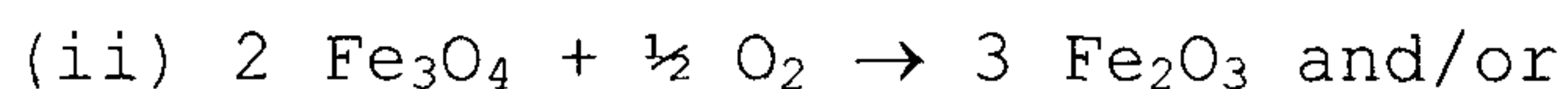
In the oxidation treatment in method step (b), therefore, an at least substantially complete reaction
30 of the various oxidation states and/or oxides of iron in the starting material to give iron(III) oxide is ensured. In particular, the reaction of the respective iron oxides to give iron(III) oxide may take place in

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accordance with the following reaction equation (ii) and/or (iii):



The reaction of iron to give iron(III) oxide is carried out in particular against the background that in accordance with the invention there is a downstream or subsequent chlorination provided in order to obtain iron(III) chloride (FeCl_3), which with respect to the regime of the invention possesses optimum sublimation properties and hence removing properties, as observed further below.

15

In the oxidation treatment in method step (b), there may also be provision for the further metals as well, especially as defined above, preferably copper, zinc, lead, cobalt, titanium, manganese, vanadium and/or chromium, more preferably copper, zinc, lead and/or cobalt, and optionally the noble metal in the form of silver, to be converted into in each case uniform oxidation states, more particularly into the in each case highest oxidation state of the metal.

25

In this context, the product mixture obtained in or after the oxidation treatment in method step (b) may comprise iron(III) oxide in amounts in the range from 10 wt% to 95 wt%, more particularly in the range from 20 wt% to 90 wt%, preferably in the range from 40 wt% to 85 wt%, based on the dry weight of the product mixture obtained in method step (b). For the purposes of the present invention, therefore, the iron oxides

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present in the starting material are converted preferably at least substantially into iron(III) oxide.

As part of the oxidation treatment, there may likewise
5 be provision for the further metals as well, more particularly copper, zinc, lead and/or cobalt, to be further oxidized, more particularly to give copper(II) oxide, zinc(II) oxide, lead(II) oxide and/or cobalt(II) oxide. This as well is useful for the subsequent
10 chlorination of these metals. Similar comments apply in respect of the metals titanium, manganese, vanadium and chromium.

Provision is made in particular in accordance with the
15 invention, therefore, for the product mixture obtained in the oxidation treatment in method step (b) to comprise the further metal in the form of the metal oxide, preferably in the form of copper(II) oxide, zinc(II) oxide, lead(II) oxide and cobalt(II) oxide.
20 The product mixture obtained in the oxidation treatment in method step (b) may in particular comprise silver oxide. Accordingly there may also, optionally, be a further oxidation of the noble metal in the form of silver as part of the oxidation treatment.

25 Furthermore, the product mixture resulting from the oxidation may comprise silicon dioxide (SiO_2) and also calcium sulfate (CaSO_4), which, so to speak, each remain at least substantially unchanged in the product
30 mixture.

With regard to the chlorination carried out subsequently as part of the method of the invention,

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particularly of the resulting oxides of iron from method step (b) and/or the oxides of the further metals resulting in method step (b), and/or, optionally, silver oxide, it is preferred in accordance with the invention if in method step (c) the chlorination is carried out as a solid phase reaction.

In this context, in method step (c), the oxidation products obtained in method step (b) and/or the product mixture obtained in the oxidation treatment in method step (b) ought to be brought to temperatures in the range from 100°C to 320°C, more particularly in the range from 150°C to 302°C, preferably in the range from 180°C to 300°C. In method step (c), in particular, the chlorination ought to be carried out at temperatures in the range from 100°C to 320°C, more particularly in the range from 150°C to 302°C, preferably in the range from 180°C to 300°C.

As far as the chlorination as per method step (c) is further concerned, it may be carried out in chlorinating devices well-known per se to the skilled person. In particular, the chlorination in method step (c) may be carried out in a chlorinating device, in particular where the chlorinating device is selected from the group of rotary kilns and drum kilns.

With further regard to the chlorination, it is especially advantageous in accordance with the invention if the procedure is such that in method step (c) iron oxide, more particularly iron(III) oxide, is converted into iron chloride, more particularly iron(III) chloride (FeCl_3).

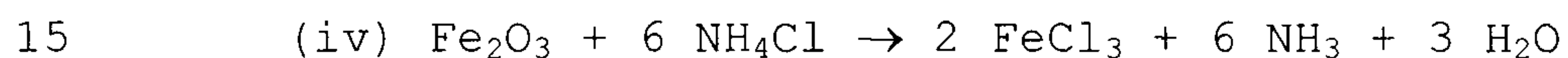
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As observed above, the iron(III) chloride or FeCl_3 which results in a preferred way has optimum removing properties in terms of the method regime of the invention, particularly in respect of the sublimation properties of iron(III) chloride.

In particular, according to one inventively preferred embodiment, whereby, as observed in detail further below, the chlorinating agent used is ammonium chloride (NH_4Cl), the conversion of iron(III) oxide into the corresponding chloride may be carried out according to the following reaction equation (iv):



Equally, in accordance with the method regime of the invention, with the chlorination of the metal oxides obtained beforehand and/or present in the product mixture, provision may be made for copper oxide, preferably copper(II) oxide, to be converted in method step (c) into copper chloride, more particularly copper(II) chloride (CuCl_2). Equally, provision may be made in method step (c) to convert zinc oxide, preferably zinc(II) oxide into zinc chloride, more particularly zinc(II) chloride (ZnCl_2). Moreover, provision may be made in method step (c) to convert lead oxide, preferably lead(II) oxide into lead chloride, more particularly lead(II) chloride (PbCl_2). Finally, provision may be made in method step (c) to convert cobalt oxide, preferably cobalt(II) oxide, into cobalt chloride, more particularly cobalt(II) chloride (CoCl_2). Moreover, in method step (c), manganese,

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particularly manganese oxide, may be converted into manganese chloride. Equally in method step (c) vanadium, more particularly vanadium oxide, may be converted into vanadium chloride. Finally, in method
5 step (c), chromium, more particularly chromium oxide, may be converted into chromium chloride.

Furthermore, in method step (c), silver oxide, preferably silver(I) oxide, may be converted into
10 silver chloride, more particularly silver(I) chloride (AgCl).

As mentioned above, it is preferred in accordance with the invention if in method step (d) there is removing
15 and/or isolating of iron chloride, more particularly iron(III) chloride (FeCl_3), from the product mixture obtained in method step (c), specifically by means of an in particular selective sublimation.

20 In this context it has in accordance with the invention emerged as being particularly advantageous if in method step d) the sublimation of iron chloride, more particularly iron(III) chloride, from the product mixture obtained in method step (c) takes place by
25 sublimation, more particularly at temperatures in the range from 200°C to 400°C, more particularly in the range from 250°C to 375°C, preferably in the range from 275°C to 350°C, more preferably in the range from 300°C to 325°C.

30

In this context, the removing or isolating of iron chloride, more particularly iron(III) chloride (FeCl_3), may be carried out in a removing device, more

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particularly sublimation device, preferably in a rotary kiln, fluidized bed kiln and/or drum kiln, into which the product mixture for purification, with the corresponding chlorides, ought to be introduced
5 beforehand.

According to one inventively preferred embodiment, as part of the present invention, a possible procedure adopted, for example, may be such that method step (c),
10 in other words the chlorination of the oxidation products obtained in method step (b), and method step (d), in other words, in particular, the removing and/or isolating of iron chloride, more particularly iron(III) chloride (FeCl_3), can be accomplished in particular
15 continuously in a common device, the common device being able more particularly to constitute a rotary kiln. In this context, the common device, more particularly the rotary kiln, may have a first section or region for implementation of method step (c), and a
20 second section or region for implementation of method step (d), more particularly for the removing and/or isolating of iron chloride, more particularly iron(III) chloride (FeCl_3).

25 In accordance with this inventive embodiment, therefore, the chlorination on the one hand and the removal of iron chloride on the other may be carried out in one and the same apparatus. As noted above, the joint apparatus is more particularly a rotary kiln,
30 this rotary kiln, along the rotary tube axis, having a first reaction region with a first temperature zone for implementing the chlorination described in method step (c), with the relevant temperatures as provided in

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accordance with the invention, and having a second sublimation region for the removing of iron chloride, with the corresponding sublimation temperatures, as described in method step (d).

5

In accordance with the invention, the desublimation in method step (d) leads, furthermore, in particular to the obtention of solid or purified iron chloride, more particularly iron(III) chloride (FeCl_3).

10

Furthermore, the reduction of iron chloride, more particularly iron(III) chloride, optionally carried out in method step d) ought in particular to take place in the gas phase, especially at temperatures in the range from 400°C to 800°C, more particularly in the range from 450°C to 750°C, preferably in the range from 500°C to 700°C, more preferably in the range from 550°C to 650°C.

20 The reduction of iron chloride, especially iron(III) chloride, may be carried out in a reduction device. Such reduction devices are well known for this purpose to the skilled person, meaning that no further observations are needed in this respect. For this purpose it is possible in particular for gaseous iron chloride to be transferred from the sublimation device into the reduction device.

30 With further regard to the method of the invention, provision may also be made for there to be a further and/or subsequent removing and/or isolation of the chlorides of the further metals from the product mixture in method step (d), in particular following

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removing and/or isolating of iron chloride, more particularly iron(III) chloride (FeCl_3).

In particular, in the context of the present invention,
5 provision may be made for method step (d), especially after removing and/or isolating of iron chloride, more particularly iron(III) chloride (FeCl_3), has taken place, to comprise further and/or subsequent removing and/or isolating of copper chloride, more particularly
10 copper(II) chloride (CuCl_2), and/or of zinc chloride, more particularly zinc(II) chloride (ZnCl_2), and/or of lead chloride, more particularly lead(II) chloride (PbCl_2), and/or of cobalt chloride, more particularly cobalt(II) chloride (CoCl_2). Similar may apply in
15 respect of titanium chloride, manganese chloride, vanadium chloride and/or chromium chloride.

For this purpose, the further or subsequent removing and/or isolating of chlorides of the further metals
20 from the product mixture may take place, for example, in a slurring or dispersing device, more particularly in a stirred tank and/or stirred reactor, preferably having at least one withdrawal means, and/or a countercurrent device, preferably having in each case
25 at least one withdrawal means.

In this context, in accordance with the invention, the procedure may for example be such that the product mixture freed in particular from iron chloride,
30 preferably iron(III) chloride (FeCl_3), is taken up, more particularly slurried and/or dispersed, in a liquid phase and/or in a liquid medium, more particularly water.

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In accordance with this aspect of the present invention, the soluble constituents of the product mixture freed in particular from iron chloride, preferably iron(III) chloride (FeCl_3), especially the chlorides of the further metals, more particularly copper chloride, preferably copper(II) chloride (CuCl_2), and/or zinc chloride, preferably zinc(II) chloride (ZnCl_2), and/or lead chloride, preferably lead(II) chloride (PbCl_2), and/or cobalt chloride, preferably cobalt(II) chloride (CoCl_2), may in particular be at least substantially completely dissolved and/or suspended, preferably dissolved. In this way, the chlorides in question of the further metals may be removed from the slurried product mixture by transfer into a suspension or solution, with a high rate of removing or purification being achievable by virtue of the good solubility or suspendability of the chlorides.

20

With regard in general to the removing of the chlorides of the further metals, it may be carried out on the basis of what is called water leaching or on the basis of what are called leaching techniques, well-known per se to the skilled person, and hence requiring no further observations.

25

In accordance with the invention, provision may be made for the resulting solution and/or suspension, preferably solution, comprising the chlorides in question to be removed from the remaining product mixture, by means for example of filtration or the like, more particularly using corresponding filter

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devices.

In this context, there may be further work-up of the resulting solution or suspension, for the especially selective removing or isolating of the chlorides of the further metals, more particularly copper chloride, preferably copper(II) chloride, (CuCl_2), and/or zinc chloride, preferably zinc(II) chloride (ZnCl_2), and/or lead chloride, preferably lead(II) chloride (PbCl_2), and/or cobalt chloride, preferably cobalt(II) chloride (CoCl_2), and/or titanium chloride, and/or manganese chloride, and/or vanadium chloride and/or chromium chloride, or to give the metallic form of the respective metal. The especially selective removing or isolating of the chlorides of the further metals and/or the conversion to the metallic form of the respective metals may be accomplished on the basis of electrochemical, sorptive, more particularly adsorptive, methods and/or by means of, in particular, selective precipitation and/or, in particular, selective sedimentation or the like. In particular, the metals can be obtained in metallic form by means of reduction. The relevant methods are well-known to the skilled person, and so no further observations are required in this regard.

With regard, therefore, to the removing or isolating of the chlorides of the further metals, a procedure in accordance with the invention is particularly such that the corresponding metal chlorides are transferred into solution and/or suspension, preferably into solution, and are therefore removed from the at least substantially insoluble constituents of the previously

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iron-freed product mixture, and the solution or suspension obtained in this way is subjected to selective removing of the chlorides of the further metals.

5

In this way, in the context of the present invention, it is also possible to remove the corresponding chlorides of the further metals from the parent product mixture based on the starting material used, and so in
10 this way, further industrially and/or technically utilizable raw materials and/or commercial products can be obtained, which are suitable, for example, for use as or in catalysts, for producing dyes and/or pigments, or the like, with the raw materials in question, in the
15 form of the chlorides of the further metals, equally possessing a high physical or product purity.

With regard to the remaining, more particularly at least substantially insoluble product mixture freed
20 from iron and also from the further metals, as defined above, this mixture also comprises, in particular, the noble metal components, more particularly gold and/or silver, and also the constituents silicon, more particularly silicon dioxide, and calcium sulfate. The
25 remaining product mixture may in particular also include silver chloride, which is virtually insoluble in water.

As a result of the upstream removing and/or isolating
30 of the iron component and also of the further metal components from the product mixture, there is a further enrichment or further concentration or an increase in the relative proportion, in particular, of the noble

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metals as well, such as gold and/or silver, in the remaining product mixture, and this is beneficial to the subsequently and optionally provided removal of the noble metals, not least in relation to the economics of the parent method and also the degrees of yield.

Hence for the purposes of the present invention, provision may be made for the product mixture obtained in method step (d), or present after method step (d) has been implemented, to comprise, calculated in each case as element and based in each case on the dry weight of the product mixture:

- gold, more particularly in amounts in the range from 1 g/t to 50 g/t, preferably in the range from 1 g/t to 40 g/t, more preferably in the range from 2 g/t to 20 g/t, very preferably in the range from 3 g/t to 15 g/t;
- silver, more particularly in amounts in the range from 2 g/t to 600 g/t, preferably in the range from 5 g/t to 500 g/t, more preferably in the range from 10 g/t to 400 g/t, very preferably in the range from 15 g/t to 200 g/t.

In accordance with the invention, for the targeted recovery of the noble metals enriched beforehand, following method step (d), it is possible to carry out a method step (e). In method step (e), the noble metal, more particularly gold and/or silver, may be removed from the product mixture obtained in method step (d) and/or from the product mixture freed from iron chloride, preferably iron(III) chloride (FeCl_3), and from the chlorides of the further metals. High yields can be achieved here as well on account of the

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preceding enrichment of the noble metals in the product mixture.

With regard to the optionally envisaged removing of the noble metal, a possible procedure, in a manner preferred in accordance with the invention, is that in method step (e) the noble metal, more particularly gold and/or silver, is removed from the product mixture taken up, more particularly slurried and/or dispersed, in a liquid phase and/or in a liquid medium, more particularly water. The removal of the noble metal, more particularly of gold and/or silver, may in particular be carried out in at least one removing and/or filter device. For this purpose, where necessary, the product mixture obtained in method step (d) may again be admixed with a dispersion medium or dissolution medium, more particularly water.

In this context it has proved advantageous in accordance with the invention if in method step (e) the noble metal, more particularly gold and/or silver, is brought or transferred, in particular at least substantially completely, into solution or suspension, more particularly into solution. This may be done, for example, by using at least one complexing component and/or complexing compound to transfer the noble metal, more particularly gold and/or silver, into solution and/or suspension, preferably solution, or contacting it in particular with the product mixture and/or with the noble metal.

Generally speaking, the complexing component or compound in question may be a substance which

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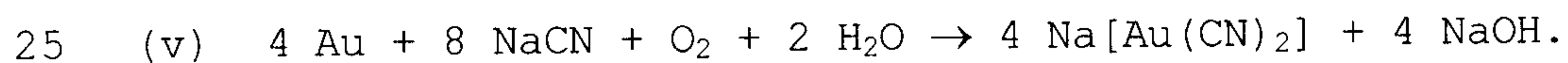
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preferably forms, with the noble metal, more particularly gold and/or silver, a complex compound which is at least substantially entirely soluble or suspendable in the dissolution medium, more
5 particularly water.

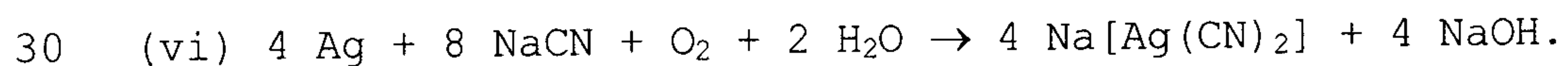
The complexing component or compound may more particularly be selected from the group of cyanide liquor, iodine/bromine solution and thiosulfate
10 solution. More particularly it is possible to use a solution of the salt of hydrocyanic acid, more particularly sodium cyanide (NaCN), as a component for transferring the noble metal into a solution and/or suspension.

15

Suitable more particularly as a relevant component, as noted above, is a sodium cyanide solution, also referred to synonymously as cyanide liquor. The reason is that as part of what is called cyanide leaching,
20 gold and/or silver are dissolved or suspended in a complex compound comprising, in particular, oxygen-containing sodium cyanide solution, especially on the basis of the following reaction equation (v):



For the noble metal in the form of silver, correspondingly, the valid reaction equation is (vi):



Subsequently there may further be provision for the resulting solution and/or suspension of the noble

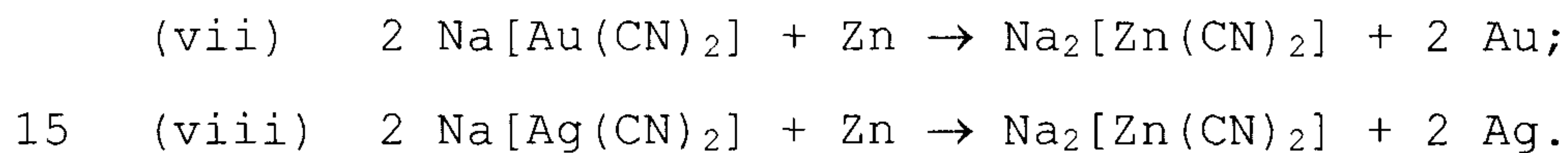
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metal, more particularly gold and/or silver, to be removed from the remaining product mixture, in particular by means of filtration, and for the noble metal, more particularly gold and/or silver, to be recovered from the solution and/or suspension, more particularly by means of precipitation methods or sorptive, especially adsorptive, methods.

For example, there may be a precipitation of the noble metal using zinc and/or aluminum, preferably in finely particulate form, more particularly on the basis of the following reaction equations (vii) and (viii):



The precipitation of the noble metal may be followed by a further filtration and purification of the crude noble metal obtained.

20

According to a further embodiment of the present invention, it is also possible to use sorptive, more particularly adsorptive, purification methods in order to obtain the noble metal, based in particular on a preferably particulate adsorption material, more particularly active carbon. For this purpose it is possible to operate with corresponding adsorption columns or the like. In principle it is also possible to employ further recovery or purification methods, such as amalgam methods and/or anode slurry methods, to obtain the noble metal.

25
30

On the basis of the method of the invention, therefore,

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efficient recovery even of noble metals, such as gold and/or silver, from the parent starting material is possible, with high yield rates being obtained in this respect, not least under the consideration that the noble metals in question are already concentrated, so to speak, in the product mixture under treatment, as a result of the upstream removal of the respective metal components. On the basis of the method of the invention, very high purities can be obtained even for the purified and isolated noble metals.

In the present invention, moreover, one particular possible approach is that the product mixture obtained in method step (d) and/or in method step (e) further comprises silicon originating from the starting material, more particularly in the form of a silicon oxide, preferably silicon dioxide. Equally, in the present invention, it may be the case that the product mixture obtained in method step (d) and/or in method step (e) further comprises at least one alkali metal and/or alkaline earth metal originating from the starting material, more particularly at least one alkaline earth metal, preferably calcium. The alkali metal or alkaline earth metal, more particularly the alkaline earth metal, preferably calcium, may be present in particular in the form of at least one salt, more particularly sulfate. In particular, the product mixture obtained in method step (d) or in method step (e) may comprise calcium sulfate originating from the starting material. Indeed, as regards the aforementioned components specifically, they are at least substantially not removed from the product mixture or chemically modified, on the basis of the

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method steps recited for the purification of the respective metal components and/or noble metal constituents, and, consequently, they are present as such at least substantially completely in the remaining
5 product mixture.

In this context, in accordance with the invention, and in relation to the remaining product mixture, it is possible to envisage in particular a further removing
10 or processing of silicon dioxide. For example, reduction to silicon may take place, based for example on the following reaction equation (ix):



15

With regard, furthermore, to the calcium sulfate remaining in the product mixture, it may be utilized as such, for the purpose of producing gypsum building materials or the like, for example.

20

In particular, the method of the invention may also be carried out using the recovery plant, defined below, according to the invention.

25 As observed above, the method of the invention is further described by the relevant co-independent method claims and dependent claims, and also by the reference to the corresponding figures.

30 All in all, therefore, on the basis of the present invention, a highly efficient method is provided for the purification or isolation, more particularly for selective and comprehensive purification or isolation,

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of metals, especially for the purpose of obtaining metallic iron, and also further metal components and optionally noble metals, such as gold and silver, more particularly from pyrite cinder, such as roasted
5 pyrites.

According to one particular embodiment of the present invention, a possible procedure is for roasted pyrites previously dried at 120°C to be subjected to oxidative
10 roasting at 700°C with the aim of converting iron into the trivalent form. Thereafter the oxidized roasted pyrites may be treated with solid ammonium chloride at a temperature of 300°C to convert iron into the chloride form, to give ammonia and water in the gas
15 phase. Subsequently, the iron chloride obtained may be removed from the product mixture by sublimation. This iron chloride is transferred into the gas phase, or sublimed, at a temperature of 950°C, with silicon dioxide and calcium sulfate and also the chlorides of
20 the further metals, and the noble metal components, remaining in the solid product mixture. The remaining product mixture has an increased noble metal content by comparison with the starting material. Iron chloride can subsequently be reduced or treated with hydrogen to
25 give metallic iron and hydrogen chloride gas. The gas streams of ammonia and hydrogen chloride can be combined for renewed formation of ammonium chloride, and reacted. From the product mixture remaining after the removal of iron chloride, the chlorides of the
30 further metals may be transferred into solution by slurring and removed. The residual product mixture thus obtained, after removal of the chlorides of the further metals, may be treated with a cyanide solution

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in order to convert gold and silver into a soluble form. The residual which remains in the purified product mixture, and which comprises a mixture of silicon dioxide (quartz) and calcium sulfate (gypsum),
5 can be removed by filtration from the solution comprising gold and/or silver. Finally, the noble metal can be obtained in the form of gold and/or silver by precipitation.

10 In the text below, the present invention on the basis of the method of the invention is elucidated in more detail using preferred working examples and figures or drawings that show embodiments. In connection with the elucidation of these preferred working examples of the
15 method of the invention, which, however, are in no way restrictive on the method of the invention, further advantages, properties, aspects and features of the present invention are also shown.

20 In the figures

fig. 1 shows a schematic representation or overview of the method of the invention for obtaining raw material from ores or ore residues, more
25 particularly for recovering metals from ores or ore residues, preferably for recovering metals from pyrite residues, more preferably from roasted pyrites obtained in the production of sulfuric acid;

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fig. 2 shows a further schematic representation or overview of the method of the invention, according to a further inventively preferred

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embodiment.

Fig. 1 schematizes one particular embodiment of the method of the invention, as will be further defined
5 below.

In particular, fig. 1 shows the regime of the invention, whereby first of all a raw material RM is present or is provided, this material more particularly
10 being an ore or an ore residue, more particularly a pyrite residue or, in particular, roasted pyrites originating from sulfuric acid production. The raw material RM comprises, in particular, iron, preferably as main constituent, and at least one noble metal, more
15 particularly gold and/or silver, and also at least one further metal, preferably selected from the group of copper, zinc, lead and cobalt, with, in particular, iron and also the further metal being present in the form of oxides.

20

In method step (a) there is a provision, more particularly processing, of a starting material AM on the basis of the parent raw material RM. The processing may comprise comminution of the raw material RM and/or
25 drying of the raw material RM to give the processed starting material AM.

After that, the starting material AM, as shown in fig. 1, is subjected as per method step (b) to an
30 oxidation treatment, which may be carried out in particular as calcining or oxidative roasting. In this context, an oxidizing agent, such as air and/or oxygen, may in particular be used. This results in a material

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OP with corresponding oxidation products, the oxidation products comprising, in particular, iron oxide and optionally oxides of the further metals. Particularly in relation to iron oxide, iron(III) oxide is obtained
5 in this context.

Fig. 1 further shows that in a further method step (c) there is a chlorination of the oxidation products, more particularly oxides, obtained in method step (b),
10 resulting correspondingly in chlorinated products CP. The chlorination of the oxides may take place by means of a recyclable chlorinating agent, especially ammonium chloride (NH_4Cl). The result on the one hand, starting from iron(III) oxide, is correspondingly iron(III)
15 chloride (FeCl_3), and, starting from the further metal oxides, corresponding chlorides of the further metals ($\text{Me}_x\text{-Cl}_y$) where $\text{Me} = \text{Cu}, \text{Zn}, \text{Pb}, \text{Co}, \text{Ti}, \text{V}$ or Cr , more particularly $\text{Cu}, \text{Zn}, \text{Pb}$ or Co).

20 The chlorinated products CP obtained by the chlorination may then be removed or isolated from the product mixture obtained in method step (c), as illustrated by fig. 1 in accordance with the method step (d) recited therein. In particular, the iron(III)
25 chloride (FeCl_3) obtained beforehand in method step (c) is sublimed in method step (d), giving gaseous iron(III) chloride ($\text{FeCl}_3(\text{g})$), which may be removed accordingly from the solid residual mixture or residue.

30 In this context, fig. 1 further shows that the resulting, especially gaseous iron(III) chloride can be desublimed on the one hand, to give solid iron(III) chloride, and that, on the other hand, the especially

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gaseous iron(III) chloride can be subjected to reduction to give metallic iron (Fe). The reaction products arising during the reduction of iron(III) chloride to metallic iron, especially in the form of an inorganic chlorine compound, preferably hydrogen chloride, may be used for the recycling of the chlorinating agent, as illustrated also schematically in fig. 1, with the inorganic chlorine compound obtained from the reduction, preferably hydrogen chloride, being reacted with reaction product resulting from the chlorinating agent in the chlorination, more particularly with gaseous ammonia (NH_3), so that in this way the chlorinating agent is obtained again in the form of ammonium chloride (NH_4Cl) which can be used again in method step (c).

Fig. 1 shows, furthermore, that in method step (d) there may also be subsequent removal of the chlorides of the further metals (Me_xCl_y), in particular downstream of the removal of iron(III) chloride. Method step (d) results in a remaining product mixture (VP), which optionally, in method step (e), as also illustrated in fig. 1, may be supplied to a further purification procedure, particularly in relation to the removal of noble metals, such as gold and/or silver. The solid product mixture remaining in method step (e) and freed from gold and/or silver comprises, in particular, calcium sulfate and silicon dioxide, and silicon dioxide, as recited in fig. 1, can be subjected to reduction to give elemental silicon.

Fig. 2 schematizes one further particular embodiment of the method of the invention, as further described

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below:

Accordingly, as set out in fig. 2, starting from a raw material such as, in particular, roasted pyrites, comprising components based on iron, copper, zinc, cobalt, gold, silver, lead, silicon and calcium, and also based on further elements, a processed starting material may be obtained by drying and comminuting.

10 The resulting starting material may be subjected to oxidation or calcining, at temperatures, for example, of 700°C, in the presence of an oxidizing agent, such as air and/or oxygen. The oxidizing treatment leads in particular to oxides of iron and of the further metals
15 being obtained, also in particular with an increase in the oxidation state of the respective metallic elements. Thus in the case of iron, for example, starting from iron(II) oxide or iron(II, III) oxide, iron(III) oxide is obtained fundamentally, in
20 accordance with the following reaction scheme:



Equally, starting for example from copper(I) oxide, copper(II) oxide is obtained fundamentally, in accordance with the following reaction scheme:



30 Similar comments apply generally in respect of the elements of the further metals.

With regard furthermore to the noble metal, especially

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gold, it is generally not oxidized as part of the oxidation treatment, owing to its noble properties. For silver as the noble metal, there may be at least partial conversion into the oxide.

5

Fig. 2 illustrates, furthermore, by way of example, the chlorination, following the oxidation, of the oxidation products obtained beforehand, using a chlorinating agent in the form of ammonium chloride (NH_4Cl), which
10 can be added to the oxidation products in solid form, in the form of a powder, for example. The chlorination may take place for example at temperatures of 300°C . The result in relation to iron(III) oxide, correspondingly, is iron(III) chloride (FeCl_3) and
15 also, purely by way of example, the result for copper oxide, correspondingly, is copper chloride (CuCl_2). Similar comments apply in respect of the oxides of the further metals. In the chlorination that is carried out, especially gaseous ammonia (NH_3) may result as a
20 reaction product originating from the chlorinating agent, especially ammonium chloride (NH_4Cl).

Fig. 2 further illustrates in this context how the resulting, in particular gaseous, ammonia (NH_3) can be
25 taken off and reacted in the gas phase with an inorganic chlorine compound, more particularly hydrogen chloride, to give recycled chlorinating agent, more particularly ammonium chloride (NH_4Cl).

30 With regard to the further procedure, the resulting chlorinating products, especially iron chloride and optionally the chlorides of the further metals, are removed from the product mixture obtained in the

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chlorination: hence fig. 2 further illustrates how iron(III) chloride (FeCl_3) are transferred into the gas phase by sublimation, more particularly at temperatures of 350°C , and so removed from the product mixture.

5

After sublimation and/or removal of iron(III) chloride, it is possible, as shown in fig. 2, for the chlorides of the further metals, such as CuCl_2 , ZnCl_2 , CoCl_2 , PbCl_2 , etc., also to be removed subsequently from the product mixture, in particular by slurring and/or dispersing of the product mixture freed from iron(III) chloride, with corresponding transfer of soluble chlorides into a solution, more particularly aqueous solution, with subsequent removal of the solution, for example by means of filtration.

10
15

With regard, furthermore, to the iron(III) chloride present as a result of sublimation and present, in particular, in the gaseous state, the method of the invention allows the operation to take place on the basis of two different variants or embodiments, as shown in fig. 2: on the one hand, the iron(III) chloride, more particularly in gaseous form, may be desublimed by desublimation to solid iron(III) chloride, to give the corresponding end product. On the other hand, iron(III) chloride, more particularly gaseous iron(III) chloride, may be subjected to reduction, in particular at 600°C , and hydrogen, for example, may be used as reducing agent. The reduction may take place in particular in accordance with the following chemical reaction equation:

$$2 \text{FeCl}_3 + 3 \text{H}_2 \rightarrow 2 \text{Fe} + 6 \text{HCl}$$

In this way, metallic iron is obtained. In the context of the present

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invention it is equally possible for both above-recited embodiments to be realized simultaneously or in parallel, for example by corresponding treatments of corresponding component streams of iron chloride.

5

Fig. 2 further illustrates how hydrogen chloride obtained during the reduction of iron(III) chloride can be taken off and used for the recycling of the above-recited chlorinating agent.

10

With regard, furthermore, to the product mixture freed from the chlorides of the aforementioned metals, it is equally possible for the noble metal, more particularly gold and/or silver, to be removed, as shown in fig. 2:

15 for example, the noble metals, such as gold and/or silver, may be converted into solution or suspension, more particularly aqueous solution or suspension, by means in particular of a complexing reaction, through the use of a corresponding cyanide liquor, for example.

20 The underlying complex-forming reaction to give, in particular, water-soluble noble metal may be run on the basis of the subsequent reaction equation:
$$\text{Em} + 8 \text{ NaCN} + \text{O}_2 + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ Na}[\text{Em}(\text{CN})_2] + 4 \text{ NaOH};$$

Em = Au or Ag.

25

Fig. 2 further illustrates how the noble metals transferred into solution or suspension, especially gold and/or silver, can be purified further by corresponding filtration or removal of the solid constituents, to give a purified noble metal solution or noble metal suspension. From this solution or suspension, the isolated noble metal, more particularly gold and/or silver, may be attained by means of

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extraction or extractive precipitation or adsorption.
In this context, fig. 2 shows, by way of example, the
underlying reaction using a precipitant such as zinc or
aluminum: $2 \text{ Na}[\text{Em}(\text{CN})_2] + \text{Fm} \rightarrow \text{Na}_2[\text{Fm}(\text{CN})_2] + 2 \text{ Em};$
5 $\text{Em} = \text{Au or Ag}$ and also $\text{Fm} = \text{precipitant (Zn or Al)}$.

With regard, furthermore, to the product mixture which
remains, it comprises, in particular, calcium sulfate
and also silicon dioxide; silicon dioxide can be
10 converted into silicon by a corresponding reduction,
using carbon as reactant, for example, as also shown in
fig. 2.

Furthermore, the present invention - according to a
15 **further** aspect of the present invention - relates to
the recovery plant of the invention, particularly for
obtaining/recovering metallic iron and/or iron
compounds, more particularly iron chloride, from ores
and/or ore residues, preferably from pyrite residues,
20 very preferably from roasted pyrites obtained in the
production of sulfuric acid, more particularly a
recovery plant for implementing the method defined
above, where the recovery plant comprises:

(a) at least one providing and/or processing device,
25 more particularly for the providing, more
particularly processing, of a starting material in
the form of at least one ore and/or ore residue,
more particularly of at least one pyrite residue,
preferably of one or more roasted pyrites obtained
30 in the production of sulfuric acid, in particular
where the starting material comprises iron, at
least one noble metal and at least one further
metal;

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- (b) at least one oxidation and/or roasting device, more particularly for the oxidation treatment, more particularly calcining and/or oxidative roasting, of the provided starting material, more particularly to give iron oxide and oxides of the further metals as oxidation products in the resulting product mixture;
- (c) at least one chlorinating device, more particularly for the chlorination of the oxidation products, more particularly oxides, in the product mixture and/or for the use of at least one chlorinating agent, more particularly recyclable chlorinating agent, preferably for the chlorination of iron oxide and optionally oxides of the further metals, more particularly to give iron chloride, preferably iron(III) chloride, and optionally chlorides of the further metals in the product mixture;
- (d) at least one removing device, especially for selectively removing and/or isolating iron chloride, preferably iron(III) chloride, from the product mixture, where the removing device is designed as a sublimation device,
- where the recovery plant, in particular after and/or downstream in the process direction of the removing device, has at least one desublimation device, especially for receiving and desubliming of, in particular, sublimed iron chloride and/or for obtaining, in particular, solid and/or purified iron chloride, in particular where the desublimation device is connected to the removing device, or

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where the recovery plant, in particular after and/or downstream in the process direction of the removing device, has at least one reduction device, more particularly for reducing, in particular, sublimed iron chloride, more particularly iron(III) chloride (FeCl_3), and for obtaining metallic iron and/or for obtaining at least one inorganic chlorine compound, more particularly hydrogen chloride (HCl), in particular where the reduction device is connected to the removing device;

where the above-stated devices, namely the providing and/or readying device, the oxidation and/or roasting device, the chlorinating device, and the removing device, are arranged downstream of one another in the process direction, in the order stated, and where the further above-stated devices, namely the desublimation device and the reduction device, are arranged as defined above.

The recovery plant of the invention is particularly suitable for use in the context of the above-described method according to the invention. In particular, the recovery plant of the invention enables on the one hand an efficient and comprehensive purification or removal of the metallic components from the parent starting material, and in this context, in particular, iron can be obtained both in metallic form, as a raw material for further use, more particularly further industrial use, and in the form of iron chloride, more particularly iron(III) chloride. In addition, on the

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basis of the recovery plant of the invention, noble metals, in the form of gold and silver, can be obtained. Furthermore, the recovery plant of the invention permits the recycling of the chlorinating
5 agent, envisaged in particular in relation to the method of the invention, which is accompanied by the corresponding economic and environmental advantages.

For the purposes of the present invention there may
10 also be provision for the recovery plant of the invention to have at least one desublimation device and at least one reduction device, each as described above, especially when simultaneous or parallel recovery both of iron chloride and of metallic iron is to be carried
15 out, in particular on the basis of the treatment of corresponding sub-streams of, in particular, sublimed iron chloride.

For further observations in this regard, in respect of
20 the recovery plant according to the invention, reference may be made to the dependent claims relating to the purification plant of the invention, and to the corresponding figures.

25 The present invention will now be particularized in more detail in relation to the recovery plant of the invention, using preferred working examples and drawings and figures that show embodiments. In connection with the elucidation of these preferred
30 working examples of the present invention, which, however, are in no way restrictive in relation to the present invention, further advantages, properties, aspects and features of the present invention will also

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be shown.

In the further figures:

5 fig. 3 shows a schematic representation or overview of
the recovery plant A of the invention,
preferably for obtaining raw material from ores
or ore residues, more particularly for
recovering metals from ores or ore residues,
10 preferably for recovering metals from pyrite
residues, more preferably from roasted pyrites
obtained in sulfuric acid production;

fig. 4 shows a further schematic representation or
15 overview of the recovery plant A of the
invention, in accordance with a further
inventive embodiment.

Fig. 3 and fig. 4 therefore schematize preferred
20 embodiments of the recovery plant A of the invention,
as will be further defined below:

In particular, fig. 3 and fig. 4 show the recovery
plant A of the invention, in particular for
25 obtaining/recovering metallic iron and/or iron
compounds, more particularly iron chloride, from ores
and/or ore residues, preferably from pyrite residues,
very preferably from roasted pyrites obtained in the
production of sulfuric acid, more particularly a
30 recovery plant A for implementing the above-defined
method in accordance with the invention, where the
recovery plant A comprises:

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- (a) at least one providing and/or processing device 1, more particularly for the providing, more particularly processing, of a starting material in the form of at least one ore and/or ore residue, more particularly of at least one pyrite residue, preferably of one or more roasted pyrites obtained in the production of sulfuric acid, in particular where the starting material comprises iron, at least one noble metal and at least one further metal;
- (b) at least one oxidation and/or roasting device 2, more particularly for the oxidation treatment, more particularly calcining and/or oxidative roasting, of the provided starting material, more particularly to give iron oxide and oxides of the further metals as oxidation products in the resulting product mixture;
- (c) at least one chlorinating device 3, more particularly for the chlorination of the oxidation products, more particularly oxides, in the product mixture and/or for the use of at least one chlorinating agent, more particularly recyclable chlorinating agent, preferably for the chlorination of iron oxide and optionally oxides of the further metals, more particularly to give iron chloride, preferably iron(III) chloride, and optionally chlorides of the further metals in the product mixture;
- (d) at least one removing device 4, especially for selectively removing and/or isolating iron chloride, preferably iron(III) chloride, from the product mixture, the removing device 4 being designed as a sublimation device,

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where the recovery plant A, in particular after
and/or downstream in the process direction of the
removing device 4, has at least one desublimation
5 device 14, more particularly for receiving and
desubliming, in particular, sublimed iron chloride
and/or for obtaining, in particular, solid and/or
purified iron chloride, in particular where the
desublimation device 14 is connected to the
10 removing device 4 (the latter in particular for
receiving, in particular, gaseous iron chloride
from the removing device 4), or

where the recovery plant A, in particular after
15 and/or downstream in the process direction of the
removing device 4, has at least one reduction
device 15, in particular for reducing, in
particular, sublimed iron chloride, more
particularly iron(III) chloride (FeCl_3), and for
20 obtaining metallic iron and/or for obtaining at
least one inorganic chlorine compound, in
particular hydrogen chloride (HCl), in particular
where the reduction device 15 is connected to the
removing device 4 (the latter in particular for
25 receiving, in particular, gaseous iron chloride
from the removing device 4);

where the above-stated apparatus 1, 2, 3, 4 are
arranged in the order indicated downstream of one
30 another in the operating direction and where the above-
stated apparatus 14, 15 are arranged as defined above.

The chlorinating device 3 may be selected in accordance

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with the invention from the group of rotary kilns and drum kilns.

As can be seen from fig. 4, the chlorinating device 3
5 may have at least one supply means 8 for the supply of
a chlorinating agent, especially ammonium chloride
(Na_4Cl). Moreover, the chlorinating device 3 may have
at least one takeoff and/or removal means 9, in
particular for the recovery and/or removing of reaction
10 products resulting from the chlorinating agent in the
chlorination of the oxidation products, more
particularly of preferably gaseous ammonia (NH_3).

Furthermore, it is also apparent from fig. 3 and fig. 4
15 that the recovery plant A can have at least one
reaction and/or condensation device 10. The reaction
and/or condensation device is used in particular for
combining or contacting and for the reaction of in
particular gaseous ammonia (NH_3) on the one hand and on
20 the other hand of at least one preferably inorganic
chlorine compound, especially hydrogen chloride (HCl),
in order to give recycled chlorinating agent,
preferably ammonium chloride (NH_4Cl).

25 The reaction and/or condensation device 10 may be
connected in particular to the chlorinating device 3,
in particular such that, preferably independently of
one another, gaseous ammonia can be guided from the
chlorinating device 3 into the reaction and/or
30 condensation means 10, and recycled ammonium chloride
can be guided from the reaction and/or condensation
means 10 into the chlorinating device 3. Moreover, the
reduction device 15 may be connected to the reaction

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and/or condensation device 10, especially for delivering an inorganic chlorine compound, more particularly hydrogen chloride (HCl), from the reduction device 15 into the reaction and/or
5 condensation device 10.

On the basis of the apparatus-related peculiarity of the deliberate use of a reaction or condensation device 10, therefore, the recovery plant A of the invention
10 permits the recycling of the chlorinating agent, namely more particularly of ammonium chloride.

In general, the reaction or condensation device 10, as schematized in fig. 3, is able to receive an inorganic
15 chlorine compound, resulting in connection with the reduction of iron chloride removed from the product mixture in the removing device 4, and this chlorine compound is used for the recycling of the chlorinating agent.

20
With regard specifically to the reaction or condensation device 10, provision may be made in accordance with the invention for this device, as shown in fig. 4, to have a supply means 11 for supplying
25 and/or receiving especially gaseous ammonia (NH₃), and/or at least one further supply means 12 for supplying and/or receiving at least one preferably inorganic chlorine compound, especially hydrogen chloride (HCl), and/or at least one takeoff and/or
30 removal means 13, more particularly for recovering and/or removing the recycled chlorinating agent, more particularly ammonium chloride (NH₄Cl). It is of advantage in accordance with the invention here if the

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supply means 11 is connected to the takeoff and/or removal means 9 of the chlorinating device 3. It is equally an advantage if the takeoff and/or removal means 13 is connected to the supply means 8 of the chlorinating device 3. In this way, the mass transport of the products and reactants that are relevant to the chlorinating agent is made more efficient and more selective.

Furthermore, fig. 4 shows that the recovery plant A further has at least one desublimation device 14, more particularly for receiving and desubliming, in particular, sublimed iron chloride, more particularly iron(III) chloride (FeCl_3), and/or for obtaining, in particular, solid or purified iron chloride, more particularly iron(III) chloride (FeCl_3). This desublimation device 14 is connected to the removing device 4, more particularly to the means 25 of the removing device 4 for the removal or takeoff of, in particular, gaseous iron chloride, more particularly iron(III) chloride (FeCl_3). In this connection, the desublimation device 14 ought to have at least one supply means 19, more particularly for receiving, in particular, sublimed iron chloride, especially iron(III) chloride (FeCl_3), preferably from the removing device 4.

The desublimation device may be designed, for example, as a cooling and/or condensation device.

30

Fig. 4 further shows that the plant A in accordance with the invention also has at least one reduction device 15, more particularly for reducing, in

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particular, sublimed iron chloride, more particularly iron(III) chloride (FeCl_3), and for obtaining metallic iron. In this connection, the reduction device 15 is connected to the removing device 4. Furthermore, the
5 reduction device 15 ought to have at least one supply means 16, more particularly for receiving, in particular, sublimed iron chloride, especially iron(III) chloride (FeCl_3), preferably from the removing device 4.

10

As observed above, the reduction device 15 may in particular be connected to the removing device 4, more particularly for receiving iron chloride. The reduction device 15 in this case is preferably connected via the
15 supply means 16 to the means 25 for the removal and/or takeoff of, in particular, sublimed iron chloride, more particularly iron(III) chloride (FeCl_3).

With further regard to the reduction device 15, it may
20 have at least one further supply means 17 for supplying and/or receiving a reducing agent, more particularly hydrogen or natural gas (especially methane).

In particular, moreover, the reduction device 15 may be
25 connected to the reaction and/or condensation device 10, in particular for delivering an inorganic chlorine compound, more particularly hydrogen chloride, that is produced in the course of the reduction of iron chloride, and for receiving it into the reaction and/or
30 condensation device. In this connection, the reduction device 15 may have at least one withdrawal and/or exporting means 18, especially for recovering and/or removing at least one inorganic chlorine compound,

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especially hydrogen chloride (HCl), formed in the reduction of iron chloride, especially iron(III) chloride, and/or for taking off at least one inorganic chlorine compound, more particularly hydrogen chloride (HCl), formed in the reduction of iron chloride, more particularly iron(III) chloride. In particular, the takeoff means 18 ought to be connected to the supply means 12 of the reaction or condensation device 10.

10 In this way, the inorganic chlorine compound that is needed for the recycling of the chlorinating agent may be provided via the reduction of iron chloride from the very procedure on which the recovery plant is based, and may be transferred, with the recovery plant A of
15 the invention providing the constructional requirements in this respect, as observed above.

As indicated in detail in fig. 4, the providing and/or processing device 1 may furthermore and, more particularly with regard to the provision of the starting material, comprise at least one comminuting means 6, more particularly for comminuting and/or homogenizing the starting material, and/or at least one drying means 7, more particularly for drying the
20 starting material. According to one inventively preferred embodiment, the drying means 7 here may be arranged in operational direction downstream of the comminuting means 6.

30 With further regard to the inventive recovery plant A, the oxidation or roasting device 2 may be selected from the group of rotary kilns, drum kilns, fluidized bed kilns and entrained flow reactors. In particular the

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oxidation and/or roasting device 2 may have at least one means for the supply of at least one oxidizing agent, more particularly air and/or oxygen.

5 With further regard to the inventive recovery plant A, the removing device 4 is designed as a sublimation device. In particular, the removing device 4 may be a rotary kiln, fluidized bed kiln and/or drum kiln. The removing device ought also to have at least one means
10 25 for the withdrawal or takeoff of, in particular, gaseous iron chloride, more particularly iron(III) chloride.

Fig. 4 further illustrates an inventive embodiment
15 whereby the chlorinating device 3 and the removing device 4 can be combined into a common device 24.

In this connection, the common device 24 may be designed in the form of a common rotary kiln, in particular having at least two, preferably two,
20 temperature sections. In the first temperature section or in the first temperature zone, in particular, the temperature may be that needed for the chlorination of the metal components, and the chlorination of the metal
25 components in the material with the oxidation products obtained beforehand may take place by addition of the chlorinating agent; the resulting product mixture with the chlorinated metal components may subsequently be transferred into the second temperature section or into
30 the second temperature zone, where, in the second temperature section or in the second temperature zone, the temperatures present may be those required for the sublimation in particular of iron(III) chloride. In

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this connection, the common device 24 ought to have the corresponding means for the supply of the chlorinating agent and also for the takeoff of reaction products resulting from the chlorinating agent in the chlorination, more particularly ammonia (NH_3), and ought also to have at least one further means 25 for the withdrawal or takeoff of, in particular, gaseous iron chloride, more particularly iron(III) chloride (FeCl_3), as it results during the sublimation.

10

Fig. 4 shows a further embodiment of the inventive plant A, whereby the plant A further has at least one slurring or dispersing device 20, more particularly for removing and/or isolating copper chloride, especially copper(II) chloride (CuCl_2), and/or zinc chloride, especially zinc(II) chloride (ZnCl_2), and/or lead chloride, especially lead(II) chloride (PbCl_2), and/or cobalt chloride, especially cobalt(II) chloride (CoCl_2), from the product mixture freed from iron chloride, more particularly iron(III) chloride (FeCl_3).

20

In this context, the slurring or dispersing device 20 ought to be arranged in operational direction downstream from the removing device 4 and/or in operational direction upstream from the removing or filter device 5. The purpose in particular of the slurring or dispersing device 20 is to slurry or disperse the product mixture freed from iron chloride, especially iron(III) chloride (FeCl_3), with the aforementioned chlorides of the further metals being converted into a solution or into a suspension. In this regard, the slurring or dispersing device 20 may also have at least one means 26 for receiving a dispersion

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or dissolution and/or suspension medium, more particularly water, serving both to slurry the product mixture and to convert the relevant chlorides of the further metals into a solution or suspension.

5 Furthermore, the slurring or dispersing device 20 ought to have at least one withdrawal means 27 for removing the preferably aqueous solution or suspension of the chlorides of the further metals.

10 In particular, the slurring and/or dispersing device 20 may be a stirred tank or a stirred reactor or a countercurrent device, preferably having in each case at least one withdrawal means 27. The withdrawal means are used in particular for removing the preferably

15 aqueous solution or suspension of the chlorides of the further metals, removed from the product mixture.

Fig. 4 further shows an inventive embodiment whereby the plant A also has at least one adding and/or

20 supplying device 21, preferably with an adding means 22, more particularly for adding at least one complexing component for converting the noble metal, more particularly gold and/or silver, into a solution and/or suspension, preferably solution. In this

25 connection, the complexing component may be selected from the group of cyanide liquor, iodine/bromine solution and thiosulfate solution.

As far as the adding device 21 is concerned, it ought

30 to be arranged in operational direction downstream from the removing device 4, more particularly in operational direction downstream from the slurring and/or dispersing device 20, and/or in operational direction

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upstream from the removing and/or filter device 5. The purpose of the adding or supplying device 21 is in particular to receive the product mixture freed from iron chloride, especially iron(III) chloride and also
5 from the chlorides of the further metals.

In the adding or supplying device 21, by addition of the above-defined component, the noble metal present in the product mixture, more particularly gold and/or
10 silver, is converted into a solution or suspension, and in this respect water in particular is used as dissolution or suspension medium. In this connection, the adding or supplying device 21 may optionally also have at least one means for receiving the dissolution
15 or suspension medium, more particularly water.

The purpose of the adding or supplying device 21 is therefore in particular for adding and/or for contacting the component for converting the noble metal
20 into a solution and/or dispersion to or with the product mixture, in particular the slurried or dispersed product mixture, which has been freed from iron chloride, especially iron(III) chloride, and also from the chlorides of the further metals.

25

For example, the adding and supplying device 21 may be a stirred tank or the like.

Furthermore, the inventive plant A may also have at
30 least one extraction device 23, more particularly for removing and/or obtaining the noble metal, more particularly gold and/or silver, from the solution and/or suspension. In this connection, the extraction

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device may be a precipitating device and/or sorption device, more particularly adsorption device.

5 In particular, the extraction device 23 may be arranged in operational direction downstream of the removing and/or filter device 5.

10 For example, the extraction device 23 may be designed such that it has at least one means 28 for receiving a precipitant such as, in particular, particulate zinc or aluminum. The gold precipitated in this way can be removed and isolated via corresponding filter devices or sedimentation devices.

15 For the removal of the noble metal, it is also possible in general to use stirring devices, thickening devices and filtering devices, based for example on drum filters, more particularly drum vacuum filters.

20 The respective device or means of the recovery plant A of the invention may be connected to one another in order to ensure the underlying mass transport or material transport processes, via transport means that are known per se to the skilled person, based for
25 example on conveying and/or belt transport means for transporting materials that are present in solid phase, and/or pipeline means for transporting substances that are in the gas phase.

30 Furthermore, the recovery plant of the invention may optionally have at least one further device for the further processing of the, in particular, solid product mixture that remains after the removal of the noble

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metal, more particularly gold and/or silver. More particularly, the plant of the invention may have at least one device for removing silicon dioxide and/or at least one device for reducing silicon dioxide to give
5 elemental silicon.

Overall, in the present invention, with the recovery plant A according to the invention, an efficient system is provided for the processing especially of pyrite
10 cinder, such as roasted pyrites, this system allowing the selective removal or isolation of different raw materials with economic-industrial relevance. In particular, the recovery plant A of the invention permits efficient implementation of the method
15 according to the invention, especially in relation to recycling of the chlorinating agent, with reduced use of chemicals and energy overall.

The present invention relates in particular as well to
20 a recovery plant A, preferably as defined above, more particularly for obtaining/recovering metallic iron and/or iron compounds, more particularly iron chloride, from ores and/or ore residues, preferably from pyrite residues, very preferably from roasted pyrites obtained
25 in the production of sulfuric acid, more particularly a recovery plant A for implementing the method in accordance with the invention and defined above, where the recovery plant A comprises:

(a) at least one providing and/or processing device 1,
30 more particularly for the providing, more particularly processing, of a starting material in the form of at least one ore and/or ore residue, more particularly of at least one pyrite residue,

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preferably of one or more roasted pyrites obtained in the production of sulfuric acid, in particular where the starting material comprises iron, at least one noble metal and at least one further metal;

5 (b) at least one oxidation and/or roasting device 2, more particularly for the oxidation treatment, more particularly calcining and/or oxidative roasting, of the provided starting material, more particularly to give iron oxide and oxides of the further metals as oxidation products in the resulting product mixture;

10 (c) at least one chlorinating device 3, more particularly for the chlorination of the oxidation products, more particularly oxides, in the product mixture and/or for the use of at least one chlorinating agent, more particularly recyclable chlorinating agent, preferably for the chlorination of iron and optionally of the further metals, more particularly to give iron chloride, preferably iron(III) chloride, and optionally chlorides of the further metals in the product mixture,

15 where the recovery plant A has at least one reaction and/or condensation device 10, more particularly for combining and/or contacting and for reacting, in particular, gaseous ammonia (NH_3) on the one hand and at least one preferably inorganic chloride compound, more particularly hydrogen chloride (HCl), on the other hand, to give recycled chlorinating agent, preferably ammonium chloride (NH_4Cl), in particular where the reaction and/or condensation device 10 is

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connected to the chlorinating apparatus 3 (the latter in particular for receiving ammonia (NH_3) from the chlorinating device 3 and in particular for delivering recycled chlorinating agent, more particularly ammonium chloride, into the chlorinating device 3);

(d) at least one removing device 4, more particularly for the selective removing and/or isolating of iron chloride, preferably iron(III) chloride, from the product mixture, where the removing device (4) is designed as sublimation device, where the recovery plant A, more particularly subsequent to and/or in operating direction downstream of the removing device 4, has at least one desublimation device 14, more particularly for receiving and desubliming iron chloride, more particularly sublimed iron chloride, and/or to give, in particular, solid and/or purified iron chloride, in particular when the desublimation device 14 is connected to the removing device 4 (the latter in particular for receiving, in particular, gaseous iron chloride from the removing device 4) or

where the recovery plant A, more particularly subsequent to and/or in operating direction downstream of the removing device 4, has at least one reduction device 15, more particularly for reducing iron chloride, more particularly sublimed iron chloride, more particularly iron(III) chloride (FeCl_3), and to give metallic iron and/or to give at least one inorganic chlorine compound, more particularly hydrogen chloride (HCl), in particular where the reduction device 15 is

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connected to the removing device 4 (the latter in particular for receiving, in particular, gaseous iron chloride from the removing device 4), and/or in particular where the reduction device 15 is connected to the reaction and/or condensation device 10; (the latter in particular for delivering at least one inorganic chlorine compound into the reaction and/or condensation device 10);

10 (e) optionally at least one slurring and/or dispersing device 20, especially for subsequent removing and/or isolation of chlorides of the further metals, more particularly of copper chloride, more particularly of copper(II) chloride

15 (CuCl₂), and/or zinc chloride, more particularly zinc(II) chloride (ZnCl₂), and/or lead chloride, more particularly lead(II) chloride (PbCl₂), and/or cobalt chloride, more particularly cobalt(II) chloride (CoCl₂), from the product mixture freed

20 from iron chloride, more particularly iron(III) chloride (FeCl₃);

where the above-stated apparatus 1, 2, 3, 4, 20 are arranged in the order indicated downstream of one another in the operating direction, and where the

25 above-stated devices 10, 14, 15 are arranged as defined above.

Lastly, the present invention - according to a **further** aspect of the present invention - relates to the use of

30 a recovery plant A, more particularly as defined above, in a method for obtaining/recovering metallic iron and/or iron compounds, more particularly iron chloride, from ores and/or ore residues, preferably from pyrite

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residues, more preferably from roasted pyrites obtained in the production of sulfuric acid, more particularly as defined above.

5 Further refinements, adaptations, variations, modifications, peculiarities and advantages of the present invention are readily perceptible and realizable for the skilled person on reading the description, without departing the scope of the present
10 invention.

The present invention is illustrated using the exemplary embodiment hereinafter, which is not, however, intended in any way to restrict the present
15 invention.

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Working example:

Implementation of the method of the invention according to one preferred embodiment of the present invention:

5

The method of the invention may be carried out, according to one specific embodiment of the present invention, as described hereinafter:

10 1. Provision of the raw material:

15 Raw material used is a pyrite residue in the form of roasted pyrites originating from sulfuric acid production, in a quantity of 1000 kg. The raw material used is first subjected to drying at 120°C. A sample of the raw material is analyzed using a mass spectrometer with inductively coupled plasma (ICP; ELAN model DRC) for its elemental composition. The starting material comprises the following elemental constituents, the corresponding mass fractions being based on the
20 respective element:

Element	Mass fraction
Fe	52 wt%
Au	2 g/t
Ag	10 g/t
Cu	0.2 wt%
Zn	0.4 wt%
Pb	0.04 wt%
Co	0.01 wt%
Si	7 wt%
Ca	4.4 wt%

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5 A further analysis of the starting material used shows that 65% of the iron is present in the form of iron(II, III) oxide (Fe_3O_4) and 35% of the iron in the form of iron(II) oxide (Fe_2O_3). Moreover, silicon is present in the form of silicon oxide, and calcium in the form of calcium sulfate. The further metals, apart from gold, are in the form of their oxides.

10

The starting material obtained by drying is further processed as follows:

2. Oxidation treatment of the starting material:

15

The dried starting material is subsequently subjected to an oxidation treatment or calcining (oxidative roasting). For this purpose, the starting material is heated to a temperature of 20 700°C. The roasting, in particular, converts iron into the trivalent form, to give iron(III) oxide (Fe_2O_3). The product mixture obtained is further analyzed for its composition. The product mixture obtained after the oxidation treatment comprises 25 iron now at least substantially completely in the form of iron(III) oxide (Fe_2O_3). The remaining metals, apart from gold and calcium, are in the form of oxides, more particularly in the highest oxidation state of the respective metals.

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3. Chlorination of iron and of the further metals:

The oxidation products obtained above, especially

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based on iron(III) oxide, and also the oxides of the further metals, such as copper, zinc, lead and cobalt, and also silver, are subjected to a chlorination, for which purpose solid or pulverulent ammonium chloride (NH_4Cl) is added to the resulting product mixture. The resultant mixture is heated to a temperature of 300°C . At this temperature, iron(III) oxide is converted to iron(III) chloride (FeCl_3), with release of ammonia and water. The resulting gaseous ammonia is removed or drawn off and used for the recycling of the chlorinating agent, as described in section 6.).

The chlorination also results in the chlorides of the further metals, especially copper chloride, zinc chloride, lead chloride and cobalt chloride, and also, where appropriate, silver chloride (at least in part).

20

4. Removal of iron chloride and of the chlorides of the further metals from the product mixture:

For the selective sublimation of iron(III) chloride (FeCl_3), the product mixture obtained after the chlorination is heated to a temperature of 350°C , with iron(III) chloride being transferred into the gas phase and being able to be taken off or removed for corresponding further processing. Because of the sublimation temperatures different from iron(III) chloride, the chlorides of the further metals initially remain at least substantially in the solid product

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mixture. Also remaining in the product mixture are the corresponding noble metals, and also silicon dioxide and calcium sulfate.

5 The chlorides of the further metals are subsequently removed from the remaining product mixture by slurring or dispersing of the product mixture in water, with the chlorides of the further metals (substantially with the exception
10 of silver chloride) going into solution in water, on account of their good solubility properties, and in this way being removed or isolated. The chlorides of the further metals, isolated in this way, may be separated further, by means of
15 selective sedimentation or precipitation, or on the basis of electrochemical or sorptive techniques, more particularly adsorptive techniques, for example. In particular, from the chlorides isolated in this way, it is also
20 possible to obtain the metals as such (by reduction, for example). In this way, in particular, the metals copper, zinc, cobalt and lead are removed, while the noble metals (gold and silver) remain in the solid residue on account of
25 their insolubility.

An analysis conducted for the remaining product mixture reveals that on the basis of the procedure according to the invention, the amount of iron and
30 also of the further metals in the remaining product mixture or residue can be reduced by more than 90%. This results equally in a concentration or enrichment of the noble metal components,

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especially of gold and/or silver, in the remaining product mixture. Hence, in relation to the remaining product mixture, freed both from iron chloride and from the chlorides of the metals, it is possible to find a gold content of around 6 g/t and a silver content of around 30 g/t (whereas the starting material contains about 2 g/t gold and 10 g/t silver).

10 5. Processing of iron(III) chloride (FeCl₃):

The iron chloride removed before by sublimation can be desublimed, according to one first variant of the method of the invention, with cooling, to give solid iron(III) chloride (FeCl₃). The resulting iron(III) chloride (FeCl₃) has a very high purity and can be marketed as a corresponding commercial product.

20 According to a second variant of the method of the invention, the sublimed iron(III) chloride may be subjected to reduction to give metallic iron. For this purpose, iron(III) chloride (FeCl₃) is reacted with a reducing agent in the form of hydrogen in the gas phase at temperatures of 600°C. This results in metallic iron and also hydrogen chloride. The resulting hydrogen chloride is removed or taken off for the recycling of the chlorinating agent, as described in section 6.).

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The iron obtained on reduction is further analyzed by means of x-ray fluorescence methods. The metallic iron obtained in the manner described

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above has a purity of at least 99.9%. According to this variant of the invention, therefore, high-purity metallic iron is provided as a corresponding commercial product.

5

6. Recycling of the chlorinating agent:

The gaseous ammonia resulting in the chlorination of iron oxide or of the oxides of the further metals (cf. observations in section 3.)) and drawn off is combined with the hydrogen chloride resulting from the reduction of iron(III) chloride (cf. observations in 5.)) and drawn off, and is reacted in the gas phase, thereby producing recycled ammonium chloride (NH_4Cl), which can be supplied again to the chlorinating operation in accordance with section 3.)).

10

15

7. Recovery of the noble metals:

20

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With regard to the remaining product mixture, present in solid or insoluble form and freed from iron chloride and also from the chlorides of the further metals, this mixture is subjected to a further purification, particularly for the purpose of obtaining the noble metals. Accordingly, the remaining product mixture, which optionally is again slurried or dispersed, can be admixed with cyanide liquor, thereby converting the noble metals present in the product mixture into a water-soluble form, by means of a complexation reaction. The remaining product mixture is removed from this solution by filtration. The noble metal

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components, in the form of gold and/or silver, can be obtained from the solution by precipitation methods, using zinc dust or the like, for example, to give purified or isolated gold and/or silver.

5 The yield of gold in this case, based on the starting material, is at least 90%.

8. Recovery of silicon and calcium sulfate:

10 The remaining product mixture comprises silicon dioxide, which can be subjected to reduction to give silicon, and also calcium sulfate, which can be obtained in the same way.

15 On the basis of the method of the invention, extrapolated to 100 000 t of raw material in the form of roasted pyrites, as well as the noble metals gold and silver, it is also possible to obtain about 50 000 t of metallic iron and also about 30 000 t of a

20 mixture based on silicon dioxide and calcium carbonate. With the method of the invention it is possible in particular to provide commercial products both in the form of metallic iron and in the form of iron(III) chloride. Moreover, it is possible to provide products

25 based on the chlorides of the further metals, as indicated above, and/or the metals as such (in particular by reduction). The substances obtained are notable in particular for a high purity. The method of the invention therefore permits an extensive and,

30 moreover, selective processing of roasted pyrites. Not least on account of the recycling of the chlorinating agent used in accordance with the invention, the method of the invention displays a high overall economy and

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also improved environmental qualities.

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List of reference symbols:

- A Recovery plant
- 1 Providing and/or processing device
- 5 2 Oxidation and/or roasting device
- 3 Chlorinating device
- 4 Removing device
- 5 Removing and/or filter device
- 6 Comminuting means
- 10 7 Drying means
- 8 Supplying means of the chlorinating device
- 9 Takeoff and/or removal means of the chlorinating device
- 10 Reaction and/or condensation device
- 15 11 Supplying means of the reaction and/or condensation device
- 12 Further supplying means of the reaction and/or condensation device
- 13 Takeoff and/or removal means of the reaction and/or condensation device
- 20 14 Desublimation device
- 15 Reduction device
- 16 Supplying means of the reduction device
- 17 Further supplying means of the reduction device
- 25 18 Withdrawal and/or exporting means of the reduction device
- 19 Supplying means of the desublimation device
- 20 Slurrying and/or dispersing device
- 21 Adding and/or supplying device
- 30 22 Adding means of the adding and/or supplying device
- 23 Extraction device
- 24 Common device
- 25 Means for iron chloride takeoff in the removing

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device

26 Means for receiving a dissolving and/or suspending
medium in the slurring and/or dispersing device

27 Withdrawal means of the slurring and/or
5 dispersing device

28 Means for receiving a precipitant in the
extraction device

WHAT IS CLAIMED IS:

1. A method for obtaining/recovering metallic iron and/or iron chloride from ores and/or ore residues in the form of pyrite residues,

wherein the method comprises the following method steps:

- (a) providing of a starting material in the form of at least one ore and/or ore residue, wherein the starting material comprises
 - (i) iron as main constituent and
 - (ii) at least one noble metal, selected from gold and/or silver, and also
 - (iii) at least one further metal, selected from the group of copper, zinc, lead, cobalt, titanium, manganese, vanadium and chromium;
- (b) oxidation treatment of the starting material provided in method step (a), using at least one oxidizing agent to give iron-oxide and oxides of the further metals;
- (c) chlorination of oxidation products obtained in method step (b) using at least one recyclable chlorinating agent, comprising the chlorination of iron oxide and oxides of the further metals to give iron chloride and chlorides of the further metals;
- (d) selective removing of iron chloride from a product mixture obtained in method step (c) and subsequent removing of chlorides of the further metals from the product mixture freed from iron chloride, wherein the selective removing of iron chloride takes place by sublimation of the iron chloride, and the iron chloride selectively removed in this way is obtained as such by subsequent desublimation, or the iron chloride selectively removed in this way is subjected to reduction to give metallic iron;

wherein in method step (c) the chlorination is carried out as a solid phase reaction and using ammonium chloride (NH_4Cl) as chlorinating agent, wherein the ammonium

chloride used as chlorinating agent in method step (c) is recycled by recovery of ammonia (NH_3) resulting from the chlorinating agent in the chlorination of the oxidation products and subsequent reaction of the ammonia with hydrogen chloride (HCl), wherein recycling of the ammonium chloride is carried out in a reaction- or condensation-device, and

wherein the above-stated method steps (a) to (d) are carried out in the order listed above.

2. The method as claimed in claim 1,

wherein ammonia (NH_3) and hydrogen chloride (HCl) are reacted in the gas phase to give ammonium chloride (NH_4Cl); and/or

wherein the ammonium chloride (NH_4Cl) recycled is used again in method step (c); and/or

wherein hydrogen chloride (HCl) results from the reduction of iron chloride carried out in method step (d); and/or

wherein hydrogen chloride (HCl) results from method step (d) from the reduction of iron chloride, wherein the ammonia (NH_3) resulting from method step (c) from the chlorination, on the one hand, and the hydrogen chloride (HCl) resulting from method step (d), on the other hand, are combined and reacted to give the recycled chlorinating agent in the form of ammonium chloride (NH_4Cl).

3. The method as claimed in claim 1 or 2,

wherein the metallic iron obtained in method step (d) has a purity of at least 90 wt%, calculated as element and based on the metallic iron obtained; and

wherein the starting material comprises iron in the form of at least one iron oxide; and

wherein the starting material comprises gold in the form of metallic gold; and

wherein the starting material comprises silver in the form of metallic silver and/or in the form of silver oxide.

4. The method as claimed in any one of claims 1 to 3,

wherein in method step (a) and/or before implementation of method step (b), the starting material is comminuted and/or homogenized; and/or

wherein in method step (b) the oxidation treatment is carried out as a solid phase reaction and/or wherein the oxidation treatment is carried out at temperatures in the range from 500°C to 1000°C; and/or

wherein, in the oxidation treatment in method step (b), iron is converted completely into iron(III) oxide; and/or

wherein a product mixture obtained in the oxidation treatment in method step (b) comprises iron(III) oxide in amounts in the range from 10 wt% to 95 wt%, based on the dry weight of the product mixture obtained in method step (b).

5. The method as claimed in any one of claims 1 to 4,

wherein in method step (c) the chlorination is carried out at temperatures in the range from 100°C to 320°C; and/or

wherein in method step (d) the sublimation of iron chloride from the product mixture obtained in method step (c) takes place at temperatures in the range from 200°C to 400°C.

6. The method as claimed in any one of claims 1 to 5,

wherein method step (c) and method step (d) take place continuously in a common device; and/or

wherein in method step (d) the desublimation leads to solid and/or purified iron chloride being obtained; and/or

wherein in method step (d) the reduction of iron chloride takes place in the gas phase at temperatures in the range from 400°C to 800°C; and/or

wherein a product mixture obtained in method step (d) and freed from iron chloride comprises an iron content of less than 10 wt%, calculated as element and based on the dry weight of the product mixture; and/or

wherein in method step (d) the subsequent removing of chlorides of the further metals takes place from the product mixture freed from iron chloride.

7. The method as claimed in any one of claims 1 to 6, wherein in method step (d) the subsequent removing of the chlorides of the further metals takes place such that the product mixture freed from iron chloride is taken up in a liquid phase and/or in a liquid medium.
8. The method as claimed in any one of claims 1 to 7, wherein a product mixture obtained in method step (d), calculated in each case as element and based in each case on the dry weight of the product mixture, comprises:
 - gold in amounts in the range from 1 g/t to 50 g/t;
 - silver in amounts in the range from 2 g/t to 600 g/t.
9. The method as claimed in any one of claims 1 to 8, wherein following method step (d) a method step (e) is carried out, wherein in method step (e) the noble metal is removed from a product mixture obtained in method step (d) and/or freed from iron chloride and from the chlorides of the further metals.
10. The method as claimed in any one of claims 1 to 9, wherein a product mixture obtained in method step (d) comprises silicon and/or wherein a product mixture obtained in method step (d) comprises at least one alkali metal and/or alkaline earth metal.
11. A recovery plant (A) for obtaining/recovering metallic iron and/or iron chloride from ores and/or ore residues in the form of pyrite residues;

wherein the recovery plant (A) comprises:

- (a) at least one providing and/or processing device (1) for the providing of a starting material in the form of at least one ore and/or ore residue, wherein the starting material comprises iron as main constituent, at least one noble metal, selected from gold and/or silver, and also at least one further metal, selected from the group of copper, zinc, lead, cobalt, titanium, manganese, vanadium and chromium;
- (b) at least one oxidation and/or roasting device (2) for the oxidation treatment of the provided starting material to give iron oxide and oxides of the further metals as oxidation products in the resulting product mixture;
- (c) at least one chlorinating device (3) for the chlorination of the oxidation products in the product mixture and for the use of at least one recyclable chlorinating agent for the chlorination of iron oxide and oxides of the further metals to give iron chloride and chlorides of the further metals in the product mixture, wherein the chlorination is carried out as a solid phase reaction and using ammonium chloride (NH_4Cl) as chlorinating agent, wherein the chlorinating device (3) comprises at least one supply means (8) for supplying the chlorinating agent in the form of ammonium chloride (NH_4Cl), and wherein the ammonium chloride is recycled by recovery of ammonia (NH_3) resulting from the chlorinating agent in the chlorination of the oxidation products and subsequent reaction of the ammonia with hydrogen chloride (HCl);
- (d) at least one removing device (4) for the selective removing of iron chloride from the product mixture, wherein the removing device (4) is designed as a sublimation device,

wherein the recovery plant (A), in the operating direction downstream of the removing device (4), comprises at least one desublimation device (14) for accommodating and desubliming sublimed iron chloride and/or for obtaining solid and/or purified iron chloride or

wherein the recovery plant (A), in the operating direction downstream of the removing device (4), comprises at least one reduction device (15) for reducing sublimed iron chloride and for obtaining metallic iron and/or for obtaining hydrogen chloride (HCl),

wherein the above-stated devices (1, 2, 3, 4) are arranged in the order indicated downstream of one another in the operating direction and wherein the desublimation device (14) and the reduction device (15) are arranged as defined above and wherein the plant (A) comprises at least one reaction- or condensation-device (10) for combining and/or contacting and for reacting ammonia on the one hand and hydrogen chloride on the other hand, to give recycled ammonium chloride.

12. The plant as claimed in claim 11, wherein the chlorinating device (3) comprises at least one takeoff and/or removal means (9) for the recovery of reaction products resulting from the chlorinating agent in the chlorination of the oxidation products, in the form of ammonia (NH_3); and/or

wherein the reaction- or condensation-device (10) comprises at least one supply means (11) for supplying ammonia (NH_3) and/or at least one further supply means (12) for supplying and/or receiving hydrogen chloride (HCl) and/or at least one takeoff and/or removal means (13) for recovering the recycled chlorinating agent in the form of ammonium chloride (NH_4Cl).

13. The plant as claimed in claim 11 or 12, wherein the chlorinating device (3) and the removing device (4) are combined in a common device (24).

14. The plant as claimed in any one of claims 11 to 13, wherein the plant (A) further comprises at least one slurring and/or dispersing device (20) for subsequently removing chlorides of the further metals from the product mixture freed from iron chloride; and/or

wherein the plant (A) further comprises at least one adding and/or supplying device (21) for adding at least one complexing component for the transfer of the noble metal into a solution and/or suspension, and/or wherein the plant (A) comprises at least one removing

and/or filter device (5) for the removing of the noble metal from the product mixture freed from iron chloride and optionally chlorides of the further metals; and/or wherein the plant (A) further comprises at least one extraction device (23) for obtaining the noble metal from the solution and/or suspension.

15. The use of a recovery plant, as defined in any one of claims 11 to 14, in a method for obtaining/recovering metallic iron and/or iron chloride from ores and/or ore residues in the form of pyrite residues as defined in any one of claims 1 to 10.

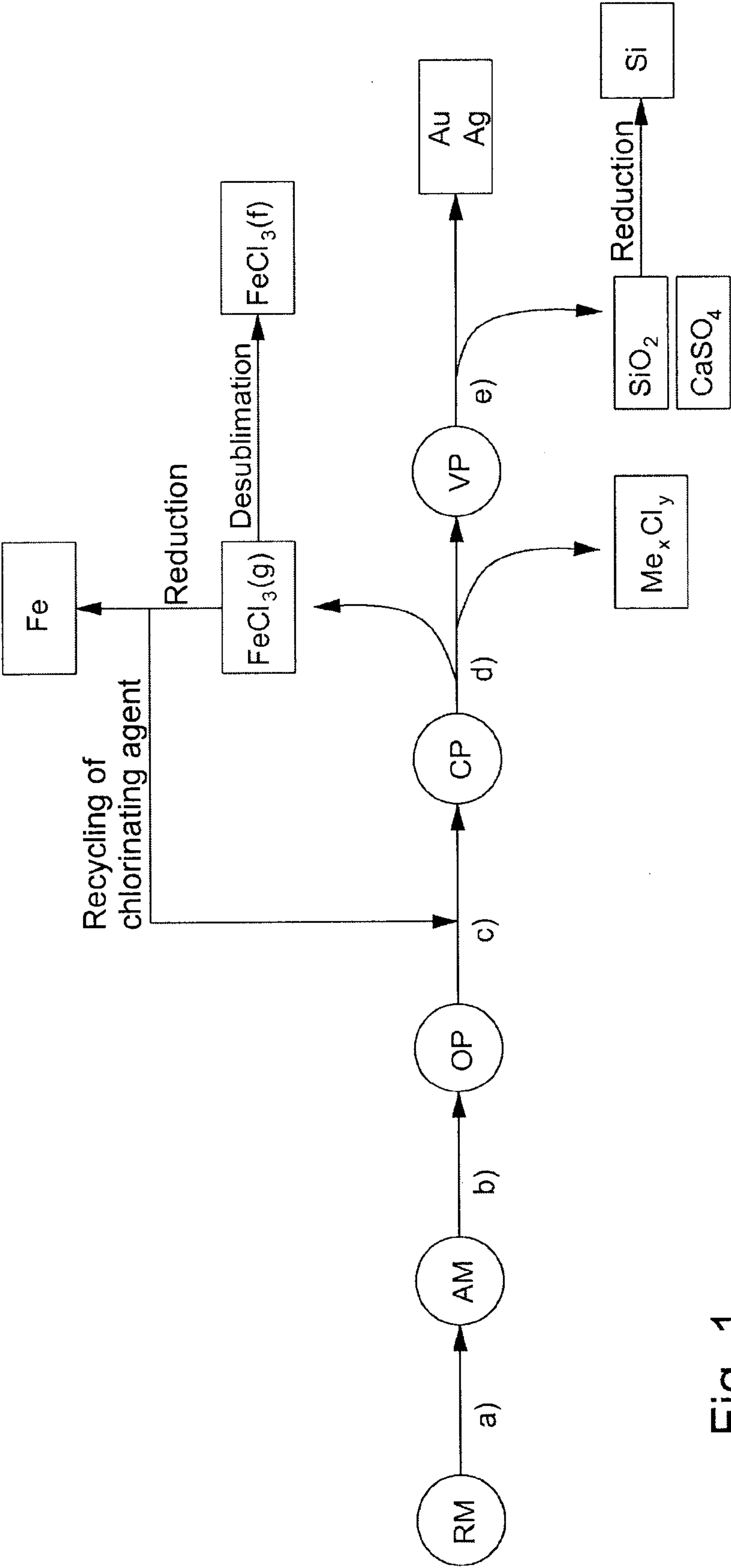
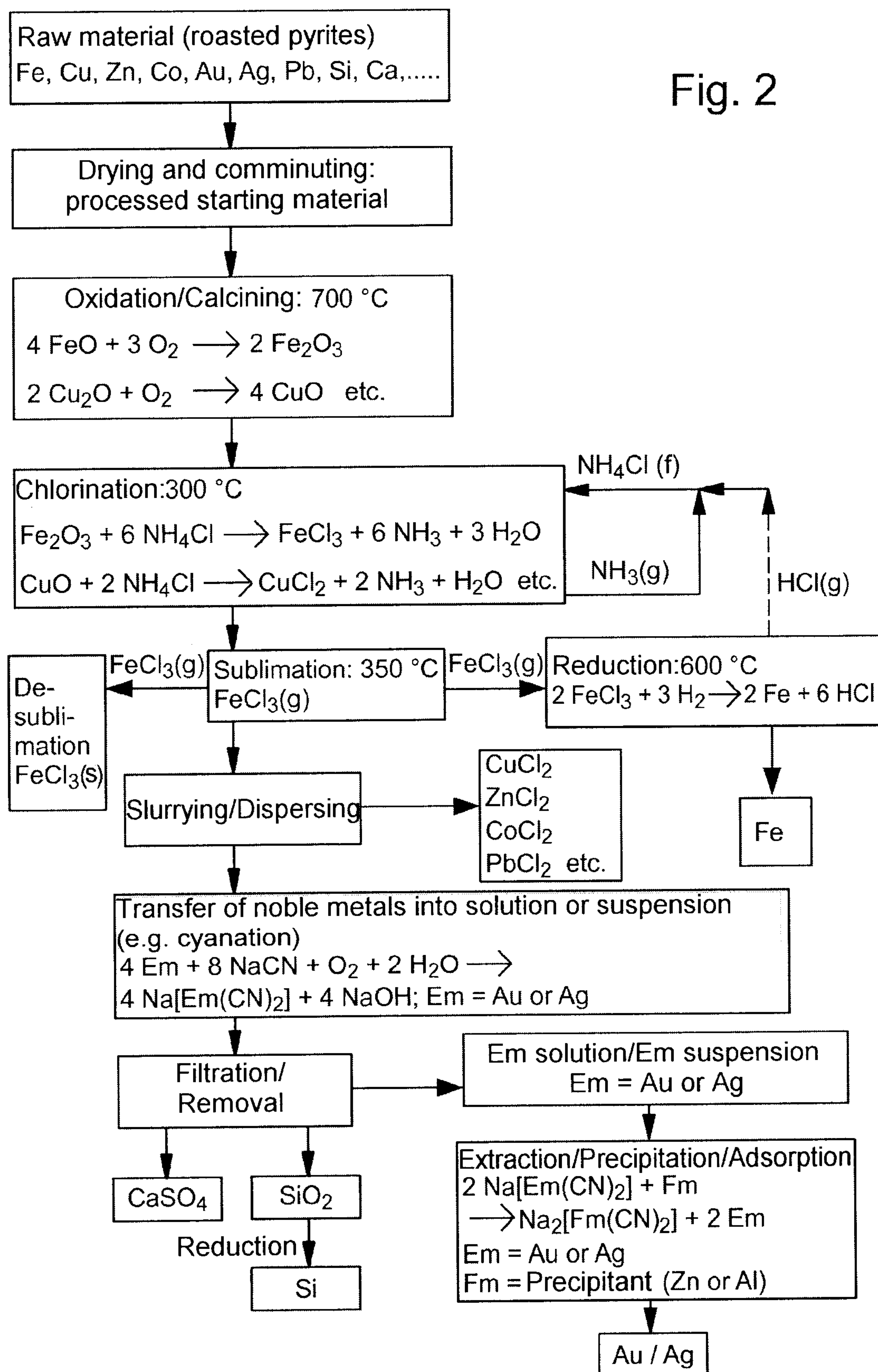


Fig. 1

Fig. 2



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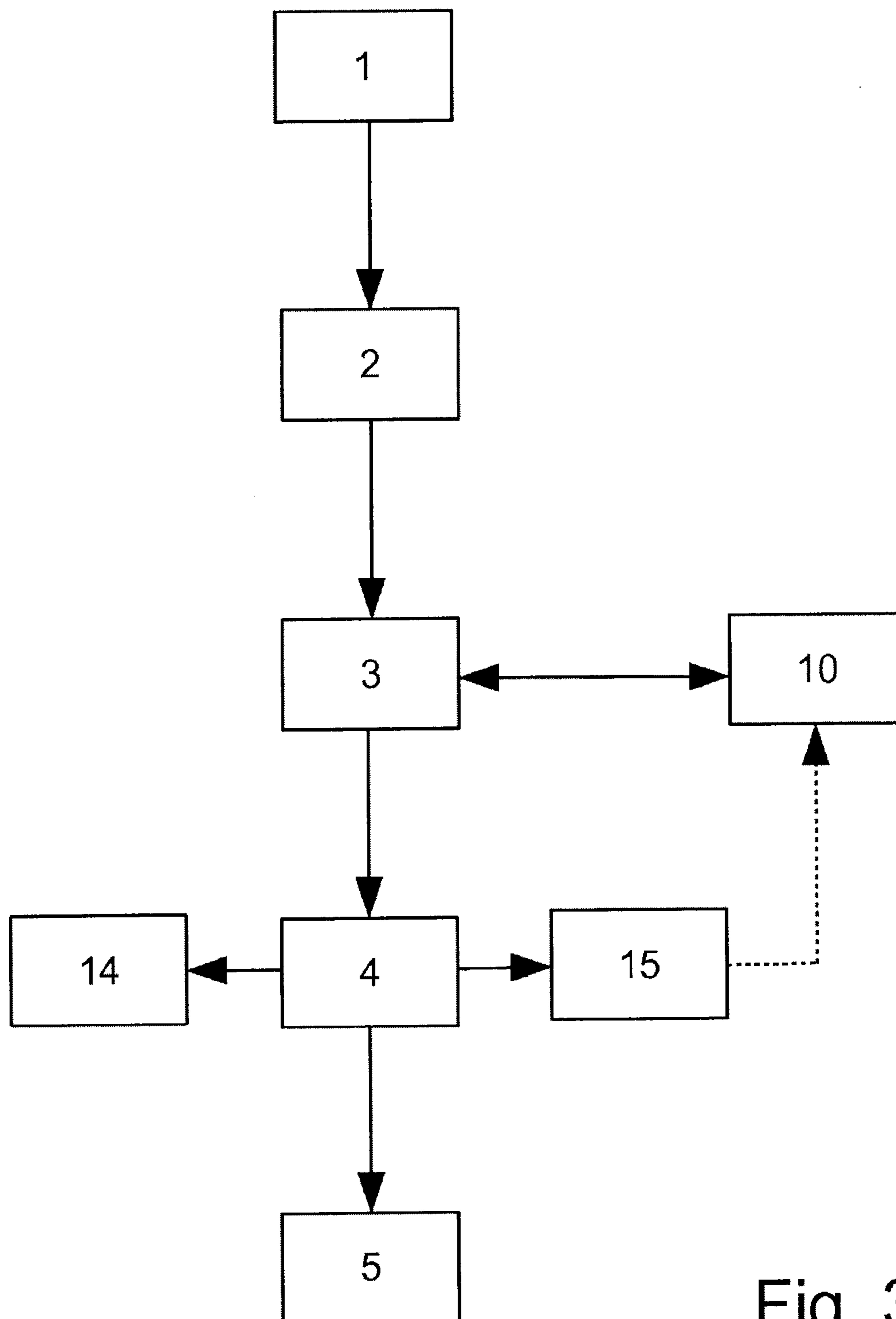
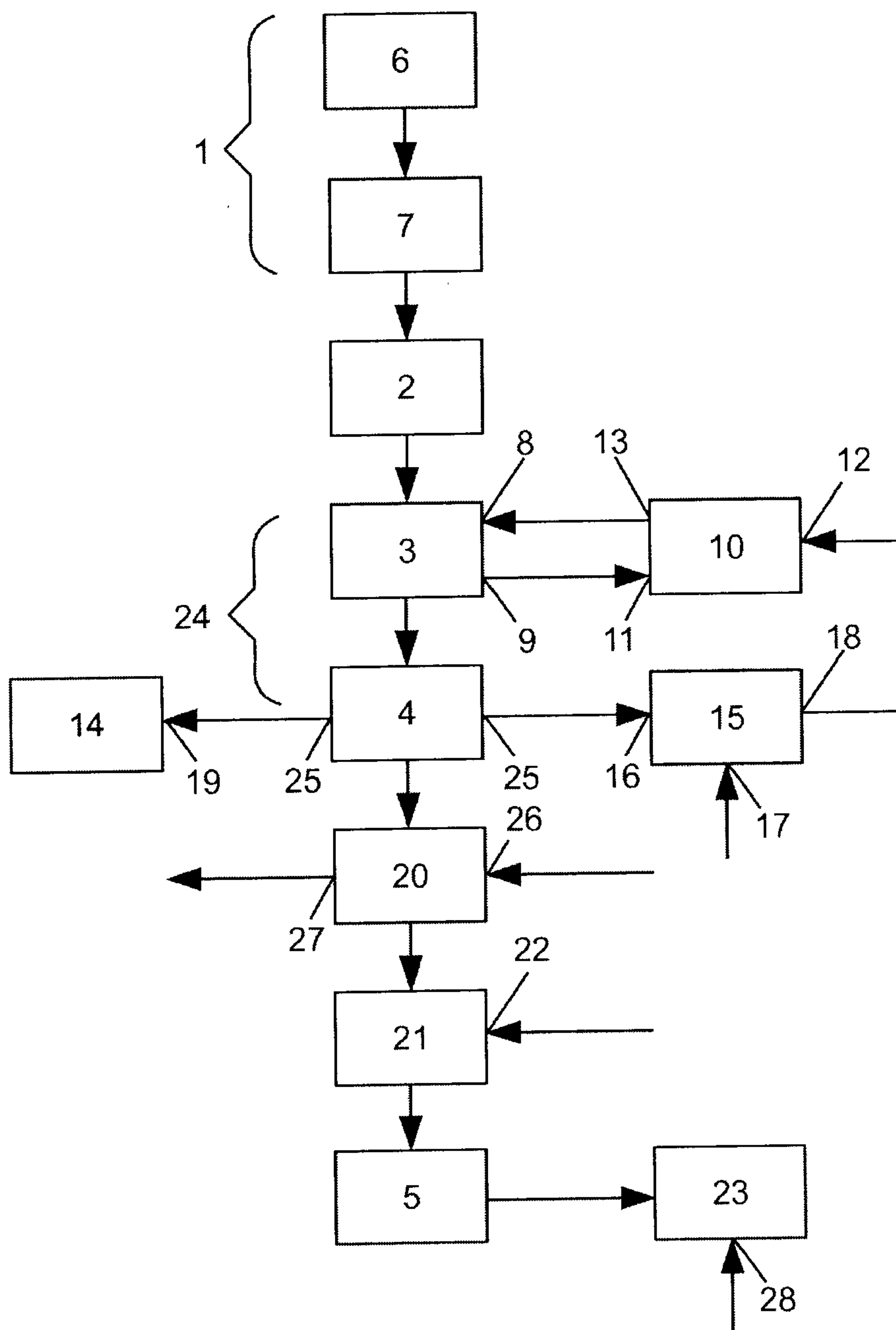


Fig. 3

**Fig. 4**

