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(54) Title: METHOD FOR UTILISING SULPHUR-CONTAINING WASTE GENERATED IN LEACHING OF SULPHIDE CONCENTRATES

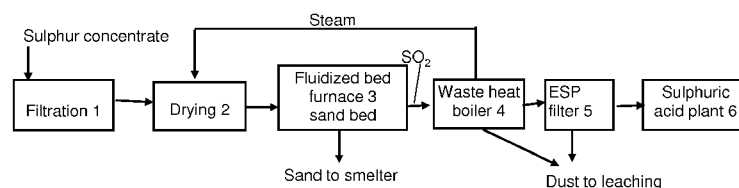


Figure 1

(57) Abstract: The invention relates to a method for treating the leaching residue containing iron and sulphur that is generated in the leaching of a sulphidic non-ferrous metal concentrate. The sulphur-containing leaching residue or part of it is routed to fluidized bed treatment, in which the sulphur contained in the leaching residue is burnt to form sulphur dioxide and the valuable metals contained in the leaching residue are recovered, mostly as oxides, and routed to a metal recovery process.

METHOD FOR UTILISING SULPHUR-CONTAINING WASTE GENERATED IN LEACHING OF SULPHIDE CONCENTRATES

FIELD OF THE INVENTION

- 5 The invention relates to a method for processing waste containing iron and sulphur i.e. leaching residue, generated in the leaching of sulphidic non-ferrous metal concentrates. Sulphur-containing leaching residue or part of it is routed to fluidized bed treatment, in which the sulphur contained in the leaching residue is burnt into sulphur dioxide and the valuable metals
10 contained in the leaching residue are recovered, mainly as oxides, and recycled to the metal recovery process.

BACKGROUND OF THE INVENTION

- Hydrometallurgical treatment processes of sulphide concentrates containing
15 non-ferrous metals, in which at least one desirable valuable metal is leached directly from the concentrate, produce wastes containing elemental sulphur and further a part of the valuable metals. The sulphide ores and concentrates in question, in addition to one or several valuable metals, generally also contain iron. Sulphur-containing wastes are generated for
20 example in the direct leaching of zinc sulphide concentrate, as the sulphide of the concentrate forms elemental sulphur in leaching. Elemental sulphur is separated from the iron deposit of the leaching residue by flotation and the sulphur concentrate that is generated contains 60 – 80% elemental sulphur. Besides sulphur, the concentrate contains the sulphides of various metals
25 (e.g. Fe, Zn, Pb and Cu), smaller amounts of sulphates (Fe, Pb, Ca) and also quartz and/or silicates. Depending on the sulphide concentrate to be leached, the sulphur concentrate may even include more valuable metals, such as silver for example.
- 30 Non-ferrous metal sulphide concentrates are also processed pyrometallurgically by the fluidized bed technique: partially roasting copper-containing sulphide concentrates at a temperature of around 600°C, treating

5 sulphides containing Co, Ni, Cu and Fe with selective sulphation roasting at a temperature of around 680°C, and dead roasting zinc sulphides at a temperature of 900 – 950°C. During roasting, the sulphides are oxidised into either sulphates or oxides depending on the roasting method used. When oxides are formed in roasting, the sulphur contained in the sulphide is oxidised into sulphur dioxide and is usually routed to sulphuric acid production, if its concentration in the gas is sufficient for economic production.

10 When a roaster, particularly one for the roasting of sulphidic non-ferrous metal concentrate, is ramped up after a shutdown, heating is done in several stages. The first stage is generally carried out with oil burners to a temperature of about 400°C and then to a temperature of about 800°C with either oil or coal. In this case, using fossil fuels generates gases containing
15 CO₂, which also contain impurities leaving the bed. The gas generated in heating cannot be routed to the acid plant, because its SO₂ concentration is too low.

The fluidized bed technology used in roasting is also utilised in the
20 processing of different kinds of wastes, and in this case the combustion of waste material is generally carried out by means of carbon-containing material.

It is also known in the prior art that to produce sulphuric acid, iron sulphide
25 ore is mined, which is crushed, ground and concentrated into pyrite, FeS₂, and/or pyrrhotite, FeS, which are burnt in a fluidized bed at a temperature of 800 – 850°C to produce SO₂-containing gas for sulphuric acid production. Pyrite and pyrrhotite contain mostly iron (26-46% Fe) and sulphur (30-52% S). In combustion purple ore is produced, which mainly ends up as waste,
30 because it contains impurities that prevent its utilisation.

The methods mentioned above are not environmentally sound in every respect, since direct leaching of sulphide concentrate gives rise to a sulphur-containing leaching residue, which is a waste that requires its own separate storage area. When waste is incinerated using carbon-containing materials, on the other hand, carbon dioxide is generated that has to be removed into the environment. The fabrication of sulphuric acid from pyrite requires procedures that incur their own costs and generates purple ore in treatment that has to be stockpiled.

10 PURPOSE OF THE INVENTION

The purpose of the method accordant with the invention is with different ways to make use of the sulphur-containing waste generated in the leaching of sulphide concentrates, by burning and oxidising it in a fluidized bed. Firstly, when the sulphur-containing waste generated in the leaching of sulphidic non-ferrous metals is burnt in a fluidized bed, in addition to an SO₂-containing gas, the valuable metals contained in the waste are also recovered. Secondly, the sulphur-containing waste can be used as fuel for heating the fluidized bed furnace, whereupon the sulphur dioxide concentration of the gases generated may rise sufficiently that the gases may be routed to sulphuric acid production. Additionally, the heat generated when burning sulphur is recovered in the heat recovery boiler. The further treatment of the sulphur-containing waste that takes place in the fluidized bed is environment-friendly, because it reduces the need for stockpiling and no carbon dioxide is generated in the method. Since the sulphur dioxide that is formed is routed to sulphuric acid production, less virgin ore is needed for the fabrication of sulphuric acid, whereby mining and processing costs are reduced correspondingly.

SUMMARY OF THE INVENTION

30 The essential features of the invention will be made apparent in the attached claims.

The invention relates to a method for treating the leaching residue containing iron and sulphur that is generated in the leaching of sulphidic non-ferrous metal concentrates. In accordance with the method the leaching residue is routed to fluidized bed treatment, in which the sulphur contained in the leaching residue is burnt into sulphur dioxide and the valuable metals contained in the leaching residue are oxidised into oxides or sulphates and routed to a metal recovery process.

According to one embodiment of the method, leaching residue containing iron and sulphur is treated to separate the iron and sulphur and to form a sulphur concentrate containing elemental sulphur.

According to one embodiment of the invention, the sulphur concentrate is filtered and dried and the fine-grained concentrate is routed to a fluidized bed furnace provided with a bed of sand, in which furnace the sulphur of the concentrate is oxidised into sulphur dioxide and the valuable metals into oxides or sulphates, which are recovered in conjunction with gas scrubbing from the dust of the waste heat boiler and electrostatic filter and from the sand bed.

When the sulphur concentrate is filtered and dried and routed to a fluidized bed furnace provided with a bed of sand, the sand of the sand bed that is contaminated in conjunction with roasting is fed into a non-ferrous metal smelter as slag-forming material.

According to a second and third embodiment of the invention, the sulphur concentrate is dried either only partially or routed as aqueous slurry to a fluidized bed furnace, whereby the calcine generated in the furnace during the concentrate oxydation forms a fluidized bed, in which the sulphur of the concentrate is oxidised into sulphur dioxide and the oxidised valuable metals are recovered from the calcine and from the dust of the waste heat boiler and the electrostatic filter in conjunction with gas scrubbing.

One typical sulphidic non-ferrous metal concentrate leaching process is a direct leaching process of zinc, in which the valuable metals besides zinc are silver, copper and lead.

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In a method accordant with the invention the iron in the leaching residue is sulphide or jarosite.

According to one embodiment of the invention, the sulphur concentrate is separated from the leaching residue by flotation.

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In the method accordant with the invention the temperature of the fluidized bed furnace is regulated to be in the range of 750 – 870°C and the oxygen coefficient in the range of 1.1 – 1.5.

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According to one embodiment of the method accordant with the invention, the heat generated in conjunction with the combustion of the leaching residue is used to maintain the temperature of the fluidized bed furnace and for energy production.

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According to yet another embodiment of the invention, the heat generated in conjunction with the oxidation of the sulphur concentrate is used to maintain the temperature of the fluidized bed furnace and for energy production.

25 LIST OF DRAWINGS

Figure 1 presents a flow sheet of one embodiment of the method accordant with the invention,

Figure 2 presents a flow sheet of another embodiment of the method accordant with the invention, and

30 Figure 3 is a flow sheet of a third embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The method accordant with the invention is based on the fact that sulphur-containing waste generated in the hydrometallurgical treatment of a sulphidic non-ferrous metal concentrate is utilised by burning it in a fluidized bed, whereupon a gas is formed that contains sulphur dioxide, which is suitable for the production of sulphuric acid or pure elemental sulphur. At the same time, the valuable metals remaining in the waste are separated out and turned into a form in which they can be recycled to a suitable recovery process. In fluidized bed treatment the amount of waste to be stockpiled is reduced significantly. When sulphur-containing waste is oxidised and/or burnt in a fluidized bed, it avoids the creation of carbon dioxide, which is harmful to the climate, and simultaneously produces energy for drying and heating for example. When an SO₂-containing gas is produced from waste for the production of sulphuric acid, the need to produce sulphuric acid from iron sulphide ore is reduced correspondingly.

When the term waste or sulphur-containing waste is used in the invention, it refers to the leaching residue that is generated in the hydrometallurgical fabrication of sulphidic non-ferrous metals, containing iron, sulphur and other impurities, and has to be stockpiled. Sulphur concentrate refers to the sulphur-containing material separated from the above-mentioned waste in a suitable way, such as flotation. Final waste refers to the material that has to be discarded from fluidized bed treatment, from which the sulphur and valuable metals have been removed. Final waste is made up mostly of iron oxides, quartz and silicates. Valuable metals refer not only to zinc, but also, the silver, copper and lead appearing for instance in zinc concentrates in conjunction with zinc leaching treatment.

As stated above, sulphur concentrate contains 60-80% elemental sulphur. Laboratory tests have shown that fine-grained (d₅₀ 10-18 µm) sulphur concentrate containing elemental sulphur, sulphides, sulphates, silicates and quartz, is not suitable as such for processing, for example, in conjunction

with normal zinc roasting or iron sulphide roasting. When sulphur concentrate is processed with fluidized bed technology, due to impurities such as Cu and Pb it requires its own method in which the temperature and oxygen coefficient range to be used are specified. Some alternatives are presented herein for treating waste using the method accordant with the invention.

One alternative of the method accordant with the invention is depicted in flow sheet 1. A leaching residue containing sulphur and iron is formed in the zinc fabrication process from which a sulphur concentrate containing elemental sulphur and valuable metal(s) is separated in some appropriate way, such as flotation. The separated sulphur concentrate is subjected to filtration 1 and drying 2 before fluidized bed treatment. When the sulphur concentrate is completely dried, it is fine-grained and cannot be used to form the bed in a fluidized bed furnace, so it is advantageous to use sand as the bed material. The sulphur contained in the sulphur concentrate is burnt in the fluidized bed of the furnace 3 into sulphur dioxide, which is removed from the upper section of the furnace with the fluidizing gas. The majority of the impurities contained in the sulphur concentrate exit the furnace with the gas flow and are recovered as dust from the waste heat boiler 4 and electrostatic filter ESP 5. The scrubbed gas containing sulphur dioxide is routed to the sulphuric acid plant 6. The dust of the waste heat boiler and the electrostatic filter mainly contains the zinc from the sulphur concentrate as zinc oxide or zinc sulphate, which can be routed either to the leaching stages of a zinc process or to a separate leaching process. It is advantageous to dry the sulphur concentrate with the steam obtained from the waste heat boiler.

A small amount of impurities remain in the sand bed. When the fluidized bed is regulated to operate in a narrower temperature range, such as 750 – 870°C, the proportion of material remaining in the sand bed is controlled by the temperature of the bed. For example when the temperature of the bed is about 850°C, the zinc concentration of the bed can be raised to a value of

around 15% of the mass of the bed and kept at this value by removing contaminated sand from the bed and replacing it with clean sand. The contaminated sand that is produced is recycled to a non-ferrous metal smelter, as slag-forming material in a copper smelter for instance, whereupon the silver and copper bound to the sand can be recovered along with the copper in the smelter feed. The amount of sand recycled to the smelter is minimal in relation to the total amount of slag-forming material; nor does the zinc in the recycled sand significantly raise the zinc concentration of the feed. Combustion in the fluidized bed takes place by means of air as in the roasting of zinc sulphide and pyrite, but the oxygen coefficient is regulated to be higher than in zinc sulphide roasting due to the impurities, i.e. to around 1.1 – 1.5. However, the temperature in the fluidized bed is regulated to be far lower than for instance in the normal roasting of zinc sulphide concentrate.

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Another variation of the method accordant with the invention is depicted in flow sheet 2. The sulphur concentrate generated in the zinc fabrication process is subjected to filtration 7 as in the alternative accordant with Figure 1, but drying 8 is carried out only partially. In this case too, drying is performed using steam from the waste heat boiler. The purpose of partial drying is to leave some of the moisture, for example 10 – 18%, in the sulphur concentrate, whereby the agglomerating mechanism of the moist fine-grained material can be utilised. Laboratory testing has shown that burning moist sulphur concentrate at the right temperature and the right oxygen coefficient produces a microagglomerated bed. Thus when partially-dried material is fed into the fluidized bed of the fluidized bed furnace 9, it forms micropellets there, which also act as the bed material. Therefore there is no need for a separate sand bed. As a result, the material to be removed from the bed is mostly zinc calcine, ZnO , which also includes hematite, Fe_2O_3 , and quartz, SiO_2 . The calcine can be fed directly into the leaching stages of the zinc process or into a leaching process of its own. It has been found that the amount of calcine produced is 20 – 40% of the amount of sulphur

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concentrate, and that when the calcine is fed into some zinc process leaching stage, besides zinc, lead and silver are also recovered. The gas removed from the fluidized bed is routed, in the same way as described above, via the waste heat boiler 10 and electrostatic filter 11 to the sulphuric acid plant 12. Dusts from the waste heat boiler and the electrostatic filter are also routed to zinc process leaching stages.

A third way in which the method accordant with the invention can be carried out is depicted by means of flow sheet 3. Since the sulphur concentrate generated in the zinc fabrication process has a high heat value, the concentrate does not necessarily require filtration and drying in separate stages at all; instead, the waste is fed as an aqueous slurry into the fluidized bed 13, thereby saving on the costs of filtration and drying. The moisture of the concentrate is evaporated as a result of the energy produced by oxidation and the solid material form micropellets during roasting, when operating in the right conditions with regard to temperature and oxygen pressure. The amount of zinc calcine generated in the fluidized bed is 20 – 40% of the amount of sulphur concentrate and can be routed to some zinc process leaching stage. In this method too other valuable metals in addition to zinc can be recovered, such as lead and silver. The gas containing sulphur dioxide that is generated is routed via the waste heat boiler 14 and electrostatic filter 15 to the sulphuric acid plant 16. Dusts from the waste heat boiler and the electrostatic filter are recycled to the zinc process leaching stages.

The premise in the alternatives of the method accordant with the invention described above is the approach in which sulphur concentrate is separated from an iron residue before burning the sulphur concentrate in a fluidized bed. According to a further approach accordant with the invention, the waste generated in a zinc process, which contains both iron residue and elemental sulphur, is not divided into two separate fractions, but the entire amount of waste is fed into the fluidized bed, whereupon the sulphur in the waste is

burnt to form sulphur dioxide and the metals are oxidised into oxide or sulphate. According to this alternative, the costs of flotation are also saved. The feed can be done in accordance with Figures 1 – 3 in either totally or partially dried form, or as aqueous slurry. If the iron residue is a zinc-
5 containing sulphide or jarosite, $MFe_3(SO_4)_2(OH)_6$, where M is for instance an ammonium ion or alkali metal ion, the amount of sulphur dioxide gas generated in fluidized bed treatment is significantly greater than when the feed is purely sulphur concentrate. The fluidized bed treatment results in a calcine product, which contains zinc calcine (ZnO), hematite and quartz, and
10 this product is routed to its own leaching process.

According to a further approach accordant with the invention, the dried leaching residue or sulphur concentrate replaces the oil or coal used in heating up the zinc roaster, whereby the gas containing sulphur dioxide that
15 is generated can be routed even earlier than before to the acid plant. According to this approach, both the amount of final waste to be stored and the amount of organic fuel otherwise used for heating are decreased.

In the fluidized bed treatment of sulphur concentrate or sulphur concentrate
20 and iron residue described above, the temperature used is set by the products and intermediates that form molten phases at low temperatures. At the temperatures in the fluidized bed, the metals contained in zinc concentrates form complex systems consisting of oxides and sulphides together and separately, which melt at low temperatures. In particular when a
25 sand bed is used, the amount of molten metal compounds adhering to the sand determines how much sand must be removed from the bed over function of time. The roasting of material containing different elements and different particle sizes always demands a separate temperature zone and oxygen coefficient.

EXAMPLES

Example 1

In the hydrometallurgical production of zinc, 100 000 tonnes per year of fine-grained (d_{50} 10-18 μm) sulphur concentrate is formed, which has a moisture content of 35 % H_2O . The zinc concentration of dry sulphur concentrate is in the region of 5%, which means 5 000 tonnes per year of zinc. The sulphur concentration of sulphur concentrate is around 70%. 100 000 tonnes per year of sulphur concentrate means around 12.5 tonnes per hour. The theoretical oxygen requirement for burning sulphur concentrate is about 500 Nm^3 per tonne of sulphur concentrate, which further translates into 2380 Nm^3 of air per tonne of concentrate. If it is assumed that an oxygen coefficient $\lambda = 1.5$ is used, the air requirement needed for combustion is around 45 000 Nm^3/h .

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When operating in accordance with Figure 1, sulphur concentrate is dried by means of the steam formed in the waste heat boiler and is oxidised in a fluidized bed furnace in which there is a bed of sand. Only a small part of the metals contained in the sulphur concentrate remain in the sand bed and the majority is recovered from the waste heat boiler and electrostatic filter. The temperature of the bed determines to a large extent how much zinc for instance remains in the bed of sand. When operating at a temperature of 850°C for example, the zinc concentration of the sand bed can be raised to a value of 15%. If it is assumed that 60% of the zinc remains in the sand bed, it means that in one year 20 000 tonnes of zinc-containing sand is formed. For example, a copper smelter uses sand as a slag-forming substance and the sand generated can be fed into the smelter, whereupon the copper and silver contained in it, which is generally around 0.03%, is recovered in the same way as zinc.

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When operating in accordance with Figure 2 and drying the sulphur concentrate to a moisture content of 15% H_2O , according to the research

results, in fluidizing bed conditions at a temperature of about 800°C the sulphur concentrate forms micropellets, as in normal zinc concentrate roasting, and a separate bed of sand is not required. In conjunction with the oxidation of the sulphur concentrate, zinc calcine (ZnO) is generated, which

5 also includes hematite and quartz. The amount of zinc calcine is around 30% of the amount of sulphur concentrate and can be fed into the leaching stage of the zinc recovery process. Thus the zinc and also the silver contained in the sulphur concentrate are recovered.

PATENT CLAIMS

1. A method for treating a leaching residue containing iron and sulphur generated in the leaching of a sulphidic non-ferrous metal concentrate, **characterised in that** the sulphur-containing leaching residue is routed to fluidized bed treatment, in which the sulphur contained in the leaching residue is burnt into sulphur dioxide and the valuable metals contained in the leaching residue are oxidised into oxide or sulphate and routed to a metal recovery process.
2. A method according to claim 1, **characterised in that** the leaching residue containing iron and sulphur is treated to separate the iron and sulphur and to form a sulphur concentrate containing elemental sulphur.
3. A method according to claims 1 and 2, **characterised in that** the sulphur concentrate is filtered and dried and the fine-grained concentrate is routed to a fluidized bed furnace provided with a sand bed, in which furnace the sulphur of the concentrate is oxidised into sulphur dioxide and the valuable metals into oxide or sulphate, which are recovered in conjunction with gas scrubbing from the dusts of the waste heat boiler and electrostatic filters and from the sand bed.
4. A method according to claims 1 and 2, **characterised in that** the sulphur concentrate is filtered and dried and routed to a fluidized bed furnace provided with a bed of sand, and in conjunction with roasting the sand of the contaminated sand bed is fed into a non-ferrous metal smelter as slag-forming material.
5. A method according to claims 1 and 2, **characterised in that** the sulphur concentrate is dried only partially or routed to a fluidized bed furnace as aqueous slurry, whereupon the calcine generated in the

5 furnace during the oxidation of the concentrate forms a fluidized bed, in which the sulphur in the concentrate is oxidised into sulphur dioxide, and the oxidised valuable metals are recovered from the calcine and from the dusts of the waste heat boiler and electrostatic filter in conjunction with gas scrubbing.

10 6. A method according to claim 1, **characterised in that** the sulphidic non-ferrous metal concentrate leaching process is a direct zinc leaching process.

7. A method according to claims 1 and 6, **characterised in that** the valuable metals besides zinc are silver, copper and lead.

15 8. A method according to claim 1, **characterised in that** the iron in the leaching residue is a sulphide or in jarosite form.

9. A method according to claims 1 and 2, **characterised in that** the sulphur concentrate is separated from the leaching residue by flotation.

20 10. A method according to claim 1, **characterised in that** the temperature of the fluidized bed furnace is regulated to be in the region of 750 – 870°C and the oxygen coefficient in the region of 1.1 – 1.5.

25 11. A method according to claim 1, **characterised in that** the heat generated in conjunction with the combustion of the leaching residue is used to maintain the temperature of the fluidized bed furnace and for production of energy.

30 12. A method according to claim 2, **characterised in that** the heat generated in conjunction with the oxidation of the sulphur concentrate

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is used to maintain the temperature of the fluidized bed furnace and for production of energy.

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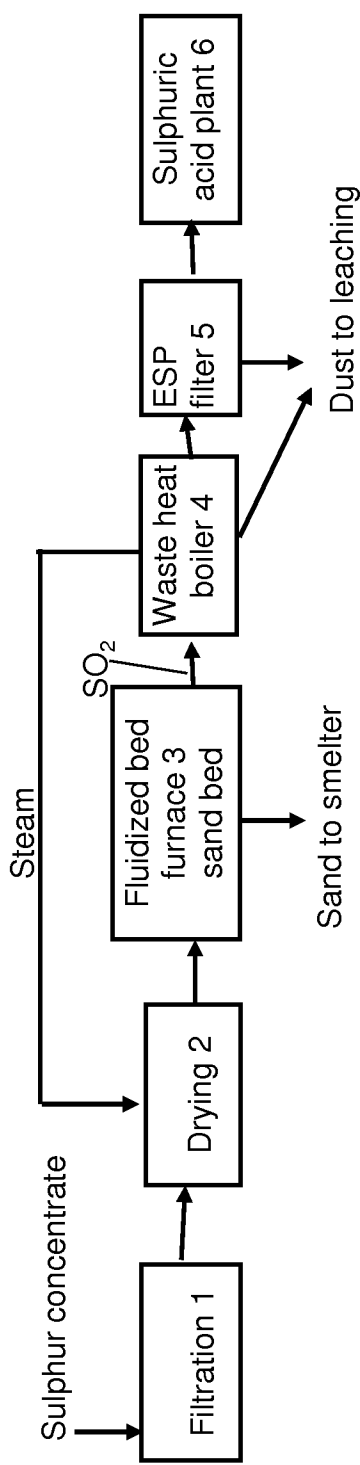


Figure 1

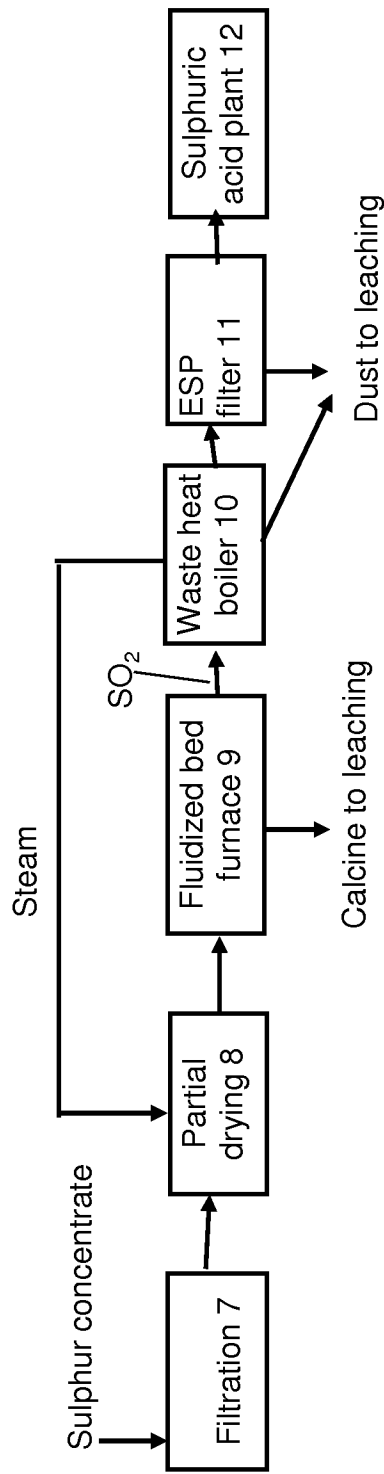


Figure 2

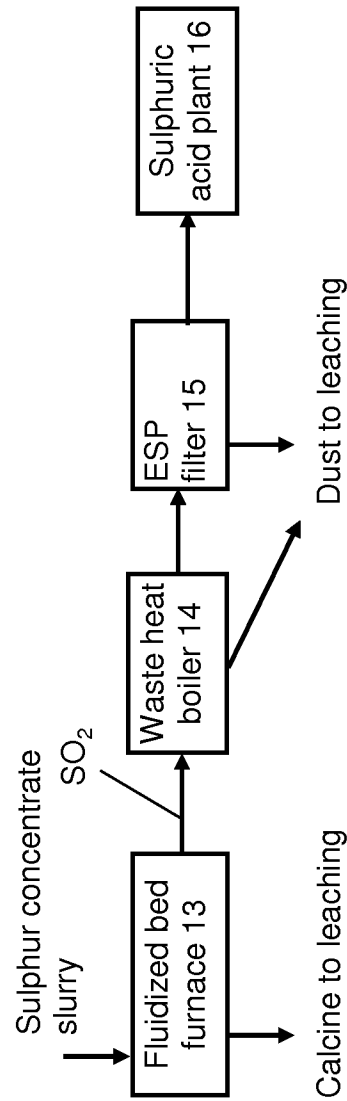


Figure 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2010/051043

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C22B, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
FI, SE, NO, DKElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4415540 A (WILKOMIRSKY IGOR A E et al.) 15 November 1983 (15.11.1983) claim 1	1 - 12
A	US 3753692 A (BOURCHIER K et al.) 21 August 1973 (21.08.1973) abstract, claim 1	1 - 12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search

30 March 2011 (30.03.2011)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2010/051043

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CLASSIFICATION OF SUBJECT MATTER

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