(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 August 2014 (28.08.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/127808 A1

(51) International Patent Classification:
*C01G 51/00* (2006.01) *C01G 3/10* (2006.01)
*C01G 51/10* (2006.01) *C22B 15/00* (2006.01)
*C01B 17/96* (2006.01) *C22B 23/00* (2006.01)

(21) International Application Number:
PCT/EP2013/053307

(22) International Filing Date:
20 February 2013 (20.02.2013)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **OUTOTEC (FINLAND) OY** [FI/FI]; Puolikkotie 10, FI-02230 Espoo (FI).

(72) Inventors: **GÜNTNER, Jochen**; Oberwaldstr. 34, 63538 Großkrotzenburg (DE). **STURM, Peter**; Deutschherrenweg 6, 61184 Karben (DE). **WROBEL, Maciej**; Am Schloss 13, 61184 Karben (DE). **HAMMERSCHMIDT, Jörg**; Sandweg 22, 63526 Erlensee (DE).

(74) Agent: **KEIL & SCHAAFHAUSEN PATENT- UND RECHTSANWÄLTE**; Friedrichstrasse 2-6, 60323 Frankfurt am Main (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17**:

— *of inventorship (Rule 4.17(iv))*

**Published**:

— *with international search report (Art. 21(3))*

WO 2014/127808 A1

(54) Title: PROCESS AND PLANT FOR PRODUCING COPPER AND/OR COBALT SULFATE

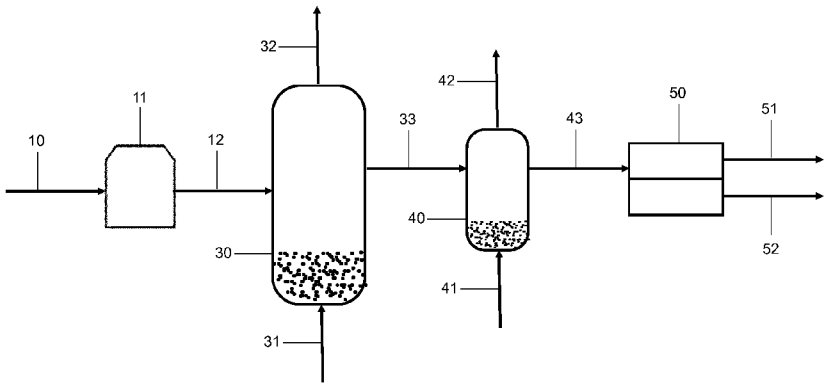


Fig. 1

(57) Abstract: The invention is directed to the production of copper and/or cobalt sulfate from copper and/or cobalt sulfide concentrates with low sulfur contents, wherein a feed stream containing copper and/or cobalt sulfide is at least partly converted to copper and/or cobalt sulfate in a roasting stage at temperatures between 600 and 7300°C and in an oxidizing atmosphere, wherein a total waste gas stream, which contains $SO_2$, is obtained and withdrawn, and wherein thermal energy and/or a sulfur-containing gas is supplied to the roasting stage as energy carrier via the feed stream and/or a fluidizing gas.

# Process and Plant for Producing Copper and/or Cobalt Sulfate

The present invention relates to the production of copper and/or cobalt sulfate from copper and/or cobalt sulfide concentrates with low sulfur content.

Copper (Cu) is a relatively soft metal and thus easily formable and tough. As an excellent conductor of heat and electricity it has a wide range of uses. In addition, copper also belongs to the group of coinage metals. It is also advantageous that as a low-reactivity heavy metal copper belongs to the semiprecious metals.

As a typical metal, cobalt (Co) likewise is a good conductor of heat and electricity (electrical conductivity about 26% of that of copper). Its use as alloying element, which leads to an increase of the wear and heat resistance of alloyed and high-alloy steels, makes it an important metal. Cobalt also is important in the production of heat-resistant colors and pigments, with cobalt being present as oxide, sulfate or hydroxide or carbonate.

Copper and/or cobalt sulfide concentrates in the sense of the present invention are understood to be minerals, e.g. ores, containing copper and/or cobalt sulfide which are found especially in the so-called 'copper belt' in Africa. They are characterized by a high amount of copper and can also contain a high cobalt content. After concentration, the concentrates have a copper content of approximately 20 to 40 wt.-% and a cobalt content of 1 to 6 wt.-%. The sulfur content was once at about 25 to 40 wt.-%

Copper and cobalt have in common that in natural occurrences they do not occur in pure form, but together with a multitude of other metals. Accompanying

metals in copper- and/or cobalt-containing ores chiefly are iron and nickel. The metals copper and cobalt in addition are present in the ores as sulfides or oxides. To recover the metals from the sulfidic compounds and in addition separate the other accompanying metals, it is known from the publication "*Sulfatizing Roasting and Leaching of Cobalt Ores at Outokumpu Oyi*" by Matti Palperi and Olavi Aaltonen, Journal of Metals, February 1971, pages 34 ff., to convert the sulfides into the corresponding sulfates by a roasting process. For this purpose, a feed stream which contains copper and cobalt in sulfidic form is introduced into a roasting process in which the exemplary following reactions take place:

$$CuS + \frac{3}{2}O_2 \rightarrow CuO + SO_2 \Delta H = -400kJ / molFU$$

$$Co_3S_4 + \frac{11}{2}O_2 \rightarrow 3CoO + 4SO_2 \Delta H = -1553\text{kJ/molFU}$$

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \Delta H = -99\text{kJ/molFU}$$

$$CuO + SO_3 \rightarrow CuSO_4 \Delta H = -218\text{kJ/molFU}$$

$$CoO + SO_3 \rightarrow CoSO_4 \Delta H = -254\text{kJ/molFU}$$

In times of increasing shortage of raw materials, cobalt and copper must be extracted, which have a lower sulfur content as it is normally used for the sulfating roasting process. As a result, enough sulfur (S) or sulfur dioxide ($SO_2$) no longer is available, in order to maintain the process with its conventional process control. Nowadays, typical copper and cobalt concentrates have a sulfur content between 8 and 20 wt.-%.

Due to the low $SO_2$ content, the aftertreatment of the waste gas stream obtained during roasting must be reconsidered. While in the past the $SO_2$ has been used to produce sulfuric acid ($H_2SO_4$), this no longer is economically expedient or even technically feasible from certain fractions since the $SO_2$-content is below 4,5 Vol.-% . Sulfur dioxide then must be removed from the waste gas stream in another way.

From EP 0 641 864 A1 it is known that when roasting refractory gold ores elementary sulfur can be used as fuel. This has the advantage that the sulfur provides the necessary energy for the roasting process and at the same time is converted to $SO_2$

$$S + O_2 \rightarrow SO_2$$

and subsequently to $SO_3$

$$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$$

by combustion according to the above reaction equation. Hence, the content of $SO_2$ in the total waste gas stream can be increased and at the same time the necessary energy can be provided.

When roasting copper and cobalt sulfides to obtain copper and cobalt sulfate, it was found out however that tight limits are set for this process. The conversion of sulfur with oxygen to sulfur dioxide is greatly dependent each on the local oxygen concentration. In a usual procedure for sulfating roasting copper and cobalt sulfides, oxygen concentrations in the waste gas between 4 and 6 Vol.-% are customary. As a result, only very small amounts of sulfur can be introduced (not more than 5 wt-% based on the total solids input), as with higher amounts of sulfur the sulfur no longer is completely converted to $SO_2$, but at least partly evaporates. This evaporation is disadvantageous, because on the one hand thermal energy is withdrawn from the process instead of being supplied, and on the other hand the evaporated sulfur is condensed out in discharge conduits of the waste gas and clogs the same. Thus, a waste gas post-cleaning here must inhibit such condensation with great expenditure, in that e.g. all conduits are

heated up to very high temperatures or a spontaneous combustion must be prevented.

It is the object of the present invention to provide a process in which copper and/or cobalt sulfides with a low sulfur content can be roasted to obtain copper and/or cobalt sulfate and at the same time a simple waste gas aftertreatment is possible.

In accordance with the invention, this object is solved by a process with the features of claim 1. For this purpose, a feed stream (feed) which contains copper and/or cobalt sulfide is supplied to a roasting stage in which the feed stream is exposed to temperatures between 600 and 730 °C in an oxidizing atmosphere and is converted to copper and/or cobalt sulfate. During roasting, there is also obtained a total waste gas stream which contains $SO_2$. According to the invention, thermal energy and/or a sulfur-containing gas is supplied to the roasting stage as energy carrier via the feed stream and/or fluidizing gas, e.g. for a fluidized bed or the like provided in the roasting stage.

Preferably, energy is supplied to the process by a fluid, wherein this amount of energy is so large that the process proceeds autothermally or exothermally. In the sense of the invention, the supply of energy can be effected by thermal energy, which causes a constant or elevated temperature in the overall system, or feeding of a sulfur-containing gas can be effected, which is converted under the reaction conditions existing in the roasting process and due to the reaction enthalpy of the respective conversion reaction thus causes a constant or elevated temperature in the overall system. Contrary to the previous procedure using a slurry feed, the educts can also be fed with a residual moisture content of only 8 - 12 wt.-% into the roasting step. This provides for an autothermal or exothermal process control.

In addition, the introduction of energy is effected such that the volume fraction of the $SO_2$ in the total waste gas stream is not decreased, i.e. remains the same or even rises. As a result, copper and/or cobalt sulfides with a lower sulfur content also can be roasted by the conventional process. The $SO_2$ content in the total waste gas stream remains sufficiently high, in order to furthermore supply the same to a plant for the production of sulfuric acid, without an expensive waste gas post-cleaning. As explained above, a waste gas stream with too low an $SO_2$ content no longer can be supplied directly to a sulfuric acid plant, but must cleaned with great expenditure. For an autothermal process in a downstream sulfuric acid plant, a $SO_2$ content of at least 4,5 Vol.% is required.

The object underlying the invention particularly preferably is solved in that $SO_2$ is fed into the roasting process in gaseous form. Restrictions of the reaction due to the $SO_2$ concentration thereby are avoided. At the same time, higher amounts of $SO_2$ are available for the strongly exothermal conversion to sulfur trioxide ($SO_3$), which is why $SO_2$ here acts as energy supplier.. This provides for a more economic mode of operation of a downstream sulfuric acid plant or allows the conventional waste gas aftertreatment in the form of a downstream sulfuric acid plant with very low sulfur contents in the feed as such.

By feeding in $SO_2$ as energy carrier, the process finally can also be controlled particularly easily, since the $SO_2$ content in the total waste gas stream can be measured continuously and this value serves as control variable for the process. The corresponding correcting variable is the supplied $SO_2$ quantity, via which not only a uniform composition of the total waste gas stream can be controlled in terms of its $SO_2$ content, but also the energy supply can be controlled.

Preferably, the $SO_2$ is generated by combustion of sulfur. This has the advantage that usual technologies for producing $SO_2$ can be employed. Since

sulfur as well as the oxygen necessary for the combustion can be provided at very low cost, this variant also is particularly economic.

The invention is particularly suitable for concentrates with a ratio of sulfur to the sum of copper and cobalt (S/(Cu+Co)) between 1:2 and 1:8. The ratio refers to the relation of the respective weight percentages. It can thereby be ensured that the process is operated autothermally or the occurring exothermicity is so low that an expensive cooling of the roasting process can be omitted.

In addition, it was found to be particularly advantageous to carry out roasting in a fluidized bed, which ensures a very good mass and heat transfer. The used grain size $d_{80}$ is between 25 and 60 µm.

When a fluidized bed is used, it was also found to be favorable to at least partly, preferably completely perform the input of energy via the fluidizing gas of the fluidized bed, as in this way the total gas quantity is not influenced and the total waste gas stream is not diluted.
When thermal energy is introduced into the system, this means that the fluidizing gas previously is heated up to such an extent that the temperature rises within the roasting system. The required amount of fluidizing gas remains constant, whereby the total waste gas stream obtained still has the same volume content of $SO_2$.

When energy is introduced by using $SO_2$ as energy carrier, this $SO_2$ likewise can be used as fluidizing gas or be admixed to the fluidizing gas. As a result, an expensive further gas introduction system can be omitted. Alternatively, $SO_2$ can also be fed together with secondary air or as a secondary air stream to avoid contact with the bottom of the fluidizing bed reactor.

Furthermore, it is possible to introduce the energy in the form of thermal energy not directly into the roasting process, but to provide a preheating of the feed, wherein this feed stream preferably is heated with hot gases and the input of energy is effected here. This preheating of the feed has the advantage that its water content of usually 25 wt-% can be lowered to 8 to 12 wt.-%. By lowering the water content, a lower evaporation enthalpy in the roasting process and thus less energy is required.

On entry into the roasting stage, the feed stream advantageously has a water content of 7 to 14 wt-%, preferably 8 to 12 wt-%. Since the water content of the concentrate can exactly be adjusted in the preheating stage, an autothermal operation of the process is facilitated. Preferably, the concentrate is filtered and the remaining filter cake is dried to a residual moisture content of 7 to 14 wt-%, preferably 8 to 12 wt-%.

When the feed stream is introduced into the roasting stage as suspension or also as fluidized particles, it can act as energy carrier itself, without having to influence fixed process parameters such as the water content.

For generating the hot gases, it was found to be advantageous to cool the copper and/or cobalt sulfate after roasting and utilize the heat obtained during cooling, in order to generate the thermal energy which then is introduced into the roasting process in gaseous form. The energy balance of the process thereby can be improved. For cooling, in particular cooling in a fluidized-bed cooler is recommendable, in which without further heat transfers a heated gas can be generated, which then can be supplied to the preheating stage and/or be used as fluidizing gas in the roasting stage. At the same time, it is of course also possible to employ a water cooling, since the same is more effective. What is also conceivable is a cooling system with several stages, wherein preferably at least the first cooling stage is designed as air cooling, preferably as fluidized-

bed cooling, and at least the last cooling stage employs water as cooling medium. The energy balance of the process also is improved when a combustion of sulfur is provided for producing $SO_2$, which utilizes this heat.

It is furthermore advantageous when roasting is effected in the presence of iron oxide and/or at least one alkali or alkaline earth metal. The iron oxide acts as catalyst for the desired reaction of $SO_2$ to $SO_3$, which provides the energy required in the process. The alkali or alkaline earth metal, on the other hand, promotes the reaction of the sulfide towards the respective oxide CuO or CoO. In general, these substances likewise are contained in the ores used as starting materials and thus in the feed, which is why a purification of the feed can be omitted..

The $SO_2$ obtained during roasting is withdrawn from the roasting process in gaseous form. Advantageously, the $SO_2$ is used as educt in a succeeding plant for the production of sulfuric acid. Hence, an expensive purification of the $SO_2$ contained in the waste gas can be omitted on the one hand, and on the other hand the economy of the process can be increased by producing a valuable product, namely sulfuric acid.

In an advantageous aspect of the invention the copper and/or cobalt sulfate obtained is dissolved in diluted acid or water after roasting. A very easy purification of these sulfates thereby can be effected, since the iron compounds obtained in the roasting process are insoluble and can easily be removed by filtration. The dissolved metals subsequently can be extracted from the mother liquor.

The invention furthermore also comprises a plant with the features of claim 13, which is suitable for carrying out the process according to the invention. Such plant for the production of copper and/or cobalt sulfate comprises an apparatus

for roasting a feed stream which contains copper and/or cobalt sulfide to obtain copper and/or cobalt sulfate, wherein during roasting the feed stream is exposed to temperatures between 600 and 7300 °C, and wherein roasting is effected in an oxidizing atmosphere. The apparatus includes means for discharging the $SO_2$ obtained during roasting from the roasting stage in gaseous form. Furthermore, the plant includes means for the input of energy in the form of thermal energy or a sulfur-containing gas. The energy input is effected such that the volume content of $SO_2$ in the total waste gas stream is not decreased.

In a particularly preferred embodiment, the roasting apparatus is designed as fluidized-bed reactor, wherein it was found to be particularly favorable when this fluidized-bed reactor is operated in at least two stages. The operation in stages offers the advantage that cooling can be effected more easily with an exothermal reaction control.

When the plant in addition includes a preheating means, preferably combined with a filter means, which also lowers the water content of the feed, the introduction of the feed preferably is effected via a slinger belt or a rotary feeder.

Advantages and further developments of the invention can also be taken from the following description of exemplary embodiments and the drawing. All features described form the subject-matter of the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

In the drawing:

Fig. 1 schematically shows a flow diagram of the process according to the invention with an energy input by thermal energy, and

Fig. 2 schematically shows a flow diagram of the process according to the invention with an energy input by means of $SO_2$ as energy carrier.

Fig. 1 schematically shows the input of energy by means of gaseous thermal energy. Via conduit 10, the feed stream (feed) which contains copper and/or cobalt sulfate in a suspension with a water content of about 25 wt-% is supplied to a preheater 11. In the same, thermal energy already can be supplied to the system via a gas stream in a non-illustrated manner. Via conduit 12, the pre-heated feed stream which due to preheating is predried to a water content of 7-14 wt-%, in particular about 10 wt-%, is introduced into the roasting reactor 30 designed as fluidized-bed reactor by means of conduit 12.

Into this fluidized-bed reactor 30 in particular sulfur-containing fluidizing gas is fed via conduit 31, which is heated such that in the ongoing process a constant temperature or an increase in temperature occurs in the reactor 30. The waste gas obtained, which contains $SO_3$, is withdrawn via conduit 32. It can then be supplied to a non-illustrated plant for producing sulfuric acid, whereby the waste gas can still be used for producing a valuable product.

Via conduit 33, the roasted solid particles, which contain copper and/or cobalt sulfate, are supplied to a cooling stage 40. Advantageously, the same is also operated with a gaseous cooling medium, in particular air. For a good heat transfer, the cooling stage favorably is designed as fluidized-bed cooling, wherein fluidizing gas is introduced via conduit 41 and the gas stream is withdrawn via conduit 42.

In a preferred aspect, the gaseous cooling stream withdrawn via conduit 41 is liberated from entrained solid particles e.g. via a non-illustrated cyclone, and the heated stream then is at least partly reused as fluidizing gas and introduced into the reactor 30 via conduit 31.

Via conduit 43, the cooled product is withdrawn from the cooling stage and at least partly dissolved in water. The admixture of water can be effected for example in a quench. While certain substances, in particular the target and valuable product copper and/or cobalt sulfate, are dissolved in water, insoluble residues, in particular iron-containing substances, remain in the solution as solids and can easily be separated. Via conduit 52, the solids are discharged from the process, whereas the copper and/or cobalt sulfate solution is withdrawn via conduit 51. For example by crystallization the valuable products then can be obtained in very pure form.

Fig. 2 schematically shows the energy input with $SO_2$ as energy carrier. Via conduit 21 solid sulfur is introduced and via conduit 20 oxygen-containing gas is introduced into the furnace 22. By combustion of sulfur, $SO_2$ is obtained here. This gas then is withdrawn via conduit 23 and for example admixed to the conduit 31, 31' for the fluidizing gases. The introduction of $SO_2$ into the reactor 30 can, however, also be effected separately and not as fluidizing gas, whereby reactor types other than a fluidized-bed reactor, e.g. a rotary kiln or a multiple hearth furnace, can also be used.

In the reactor 30, roasting of the feed containing copper and/or cobalt sulfide is effected, which is supplied to the system via conduit 13. Due to roasting, $SO_3$-containing waste gases are obtained, which can be discharged via conduit 32 and be introduced as educt into a non-illustrated plant for the production of sulfuric acid.

Via conduit 33, the roasted product, which contains copper and/or cobalt sulfate, is supplied to a cooling stage 40. This cooling stage 40 preferably is designed as fluidized-bed cooler into which the fluidizing gas is introduced via conduit 41. The waste gases are withdrawn via conduit 42 and can be utilized to at least

partly cover the energy demand of the sulfur combustion, to preheat the feed and/or to preheat the fluidizing gas.

Via conduit 43, the cooled solids are withdrawn and mixed with water in stage 50 or in a non-illustrated quench.

Copper and/or cobalt sulfate are soluble in water, whereas e.g. iron-containing substances are insoluble and thus are present in this solution as solids. By a mechanical separating operation in the separation stage 50, the solids can easily be separated and then be discharged via conduit 52, whereas copper and/or cobalt sulfate are withdrawn in solution via conduit 51. By further extraction stages, the valuable products then can be obtained in a very high degree of purity.

## List of Reference Numerals

| | |
|---|---|
| 10 | conduit |
| 11 | preheating stage |
| 12 | conduit |
| 13 | conduit |
| 20 | conduit |
| 21 | conduit |
| 22 | furnace |
| 23 | conduit |
| 30 | reactor |
| 31, 31' | conduit |
| 32 | conduit |
| 33 | conduit |
| 40 | cooling stage |
| 41 | conduit |
| 42 | conduit |
| 43 | conduit |
| 50 | liquid/solid separation stage |
| 51 | conduit |
| 52 | conduit |

**Claims:**

1. A process for producing copper and/or cobalt sulfate from copper and/or cobalt sulfide concentrates with low sulfur contents, wherein a feed stream containing copper and/or cobalt sulfide is at least partly converted to copper and/or cobalt sulfate in a roasting stage at temperatures between 600 and 7300 °C and in an oxidizing atmosphere, wherein a total waste gas stream, which contains $SO_2$, is obtained and withdrawn, and wherein thermal energy and/or a sulfur-containing gas is supplied to the roasting stage as energy carrier via the feed stream and/or a fluidizing gas.

2. The process according to claim 1, **characterized in** that $SO_2$ is supplied to the roasting stage.

3. The process according to claim 2, **characterized in** that the $SO_2$ is generated by combustion of sulfur with oxygen.

4. The process according to claim 2, **characterized in** that so much $SO_2$ is supplied to the process that the weight ratio of sulfur to the sum of copper and cobalt lies between 1:1 and 1:3.

5. The process according to any of the preceding claims, **characterized in** that roasting is effected in a fluidized bed.

6. The process according to any of the preceding claims, **characterized in** that the feed stream is preheated before entry into the roasting stage.

7. The process according to any of the preceding claims, **characterized in** that the feed stream supplied to the roasting stage has a water content of 7-14 wt-%.

8. The process according to any of the preceding claims, **characterized in** that the copper and/or cobalt sulfate is cooled after roasting and the energy obtained during cooling is at least partly recirculated into the roasting stage and/or the preheating stage.

9. The process according to any of the preceding claims, **characterized in** that roasting is effected in the presence of iron oxide and/or at least one alkali metal.

10. The process according to any of the preceding claims, **characterized in** that the $SO_2$ withdrawn is converted to $H_2SO_4$.

11. The process according to any of the preceding claims, **characterized in** that after roasting the copper and/or cobalt sulfate is dissolved in water.

12. A plant for producing copper and/or cobalt sulfate from copper and/or cobalt sulfide concentrates with low sulfur contents, comprising a roasting stage (30) for roasting a feed stream containing copper and/or cobalt sulfide at temperatures between 600 and 7300 °C in an oxidizing atmosphere for the formation of copper and/or cobalt sulfate, at least one conduit (32) for withdrawing a total waste gas stream obtained during roasting, which contains $SO_2$, and at least one means for supplying thermal energy and/or a sulfur-containing gas into the roasting stage (30).

13. The plant according to claim 12, **characterized in** that the roasting stage (30) is formed as a fluidized-bed reactor.

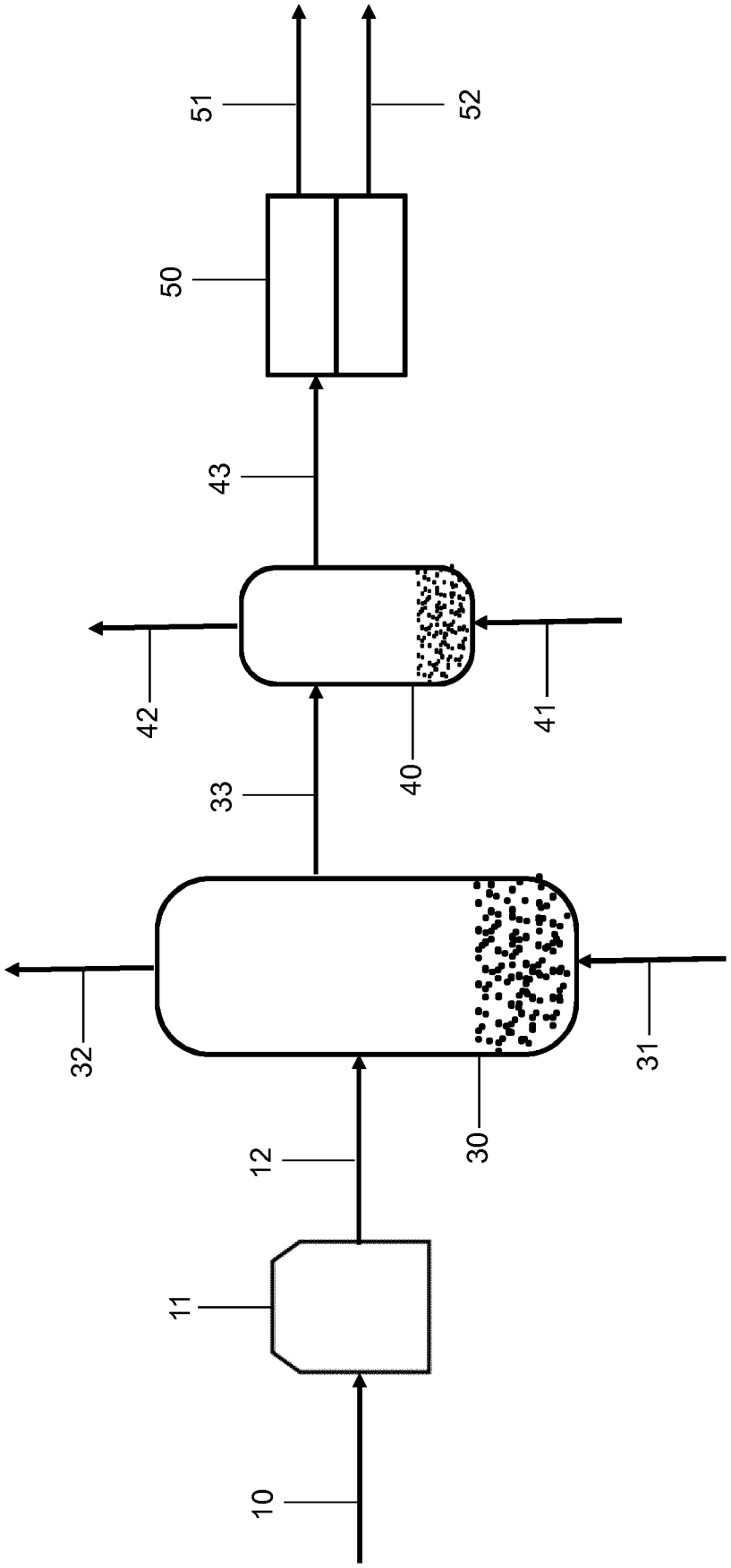


Fig. 1

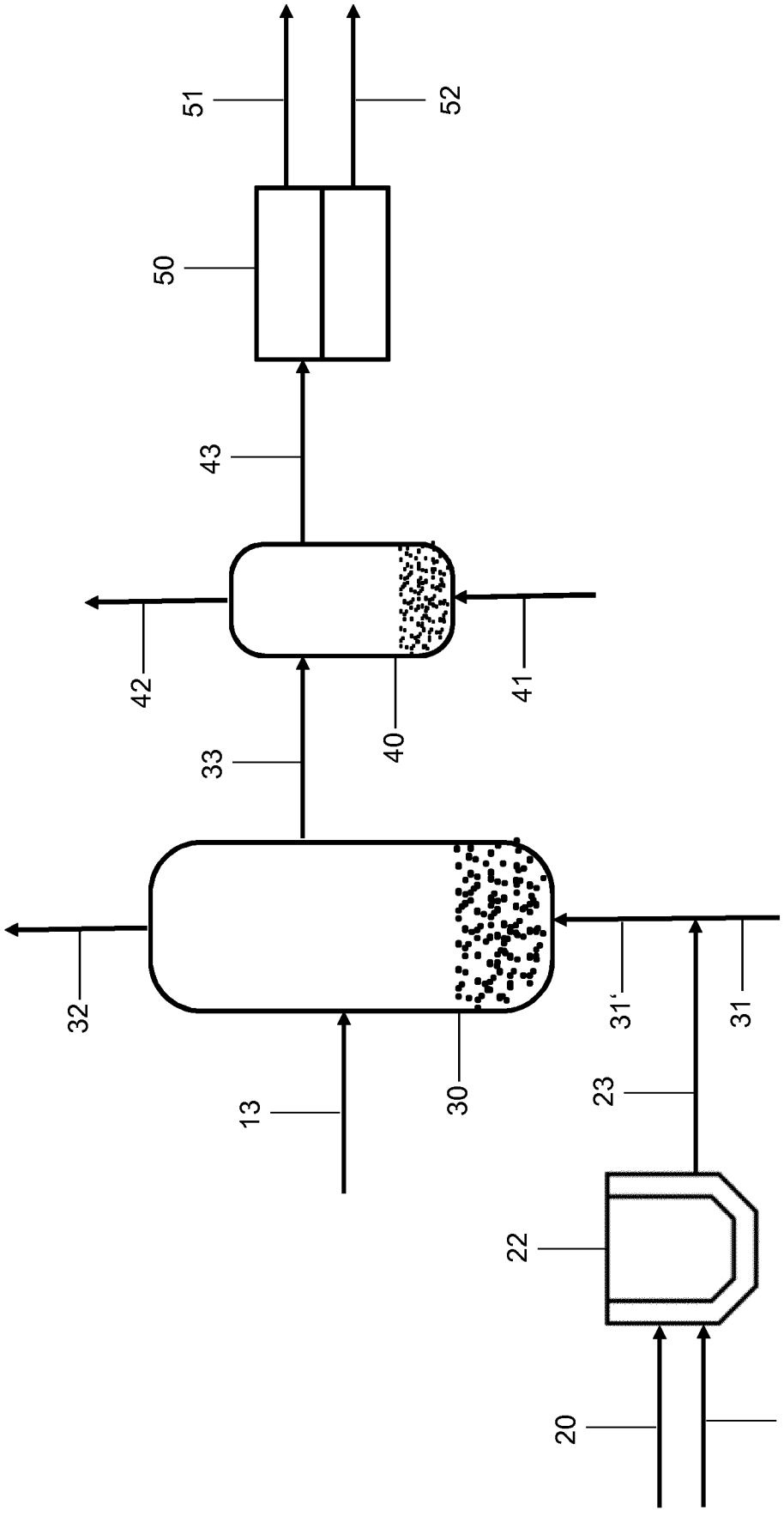


Fig. 2

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/053307

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01G51/00 C01G51/10 C01B17/96 C01G3/10 C22B15/00
C22B23/00
ADD.
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)
C01G C01B C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 30 September 2013 | 22/10/2013 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Nobis, Barbara |

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International application No
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