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(54) Title: PROCESS AND PLANT FOR CLEANING SULFUR DIOXIDE CONTAINING GAS

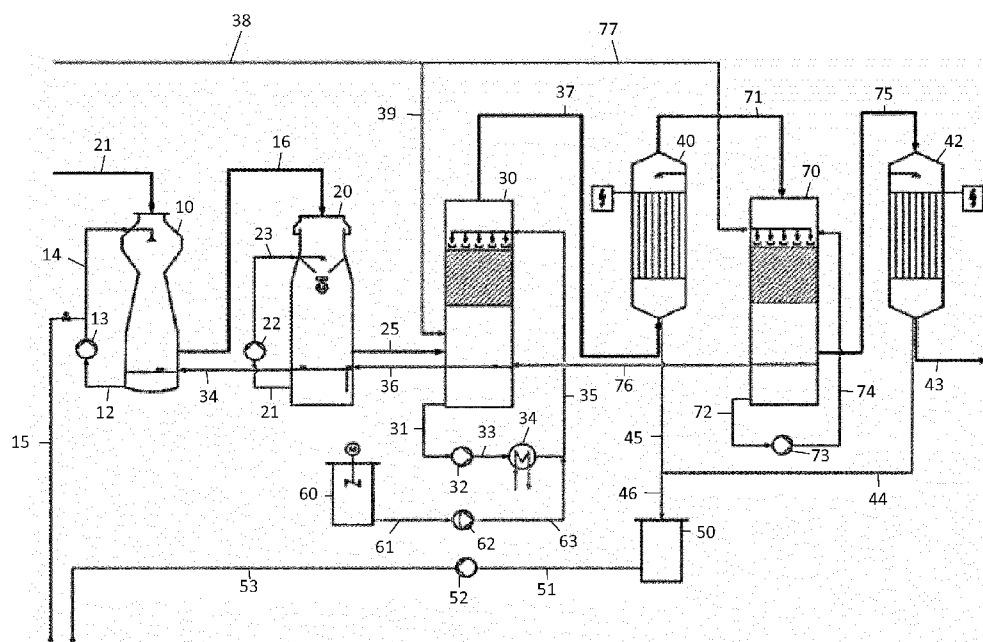


Fig. 4

(57) Abstract: The above mentioned invention describes a process for cleaning SO₂. In detail, a process gas stream containing at least 1.0 wt.-% SO₂ is quenched prior to passing into a packed bed tower and is then fed into at least one electrostatic precipitator. The condensate from the at least one electrostatic precipitator is separately withdrawn and guided into an effluent water treatment plant.

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- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

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– 1 –

Process and plant for cleaning sulfur dioxide containing gas

The invention relates to a process and its relating plant for cleaning SO₂ containing gas, wherein a process gas stream containing at least 1.0 wt.-% SO₂ is quenched before it passes a packed bed tower and is then fed into at least on electrostatic precipitator, whereby condensate from the electrostatic precipitator is guided into a liquid effluent treatment plant. SO₂-containing process gas originating from metallurgical plants treating or smelting sulfidic non-ferrous ores, are commonly processed in a hot and wet gas cleaning plant consisting of a multitude of process steps, prior to being routed to further processing and conversion to sulfuric acid.

Over the last years, a steady reduction of ore and concentrate quality is imminent, which in turn leads to an increase of impurities in the off gas. Besides metal compounds originating from the metallurgical process, those impurities are typically substances volatilized during the pyrometallurgical processing. Metal compounds containing arsenic, selenium, cadmium, mercury and the like are of particular concern.

The presence of sulfur dioxide (SO₂) and oxygen in the gas will form a certain amount of sulfur trioxide (SO₃), particularly at the presence of metal oxides which are having a catalytic effect at the prevailing high temperatures around 500 to 700 °C. At elevated temperatures and with the presence of moisture, SO₃ will mostly turn into gaseous sulfuric acid (H₂SO₄), but can also form metal sulfates.

At elevated temperatures, e.g. 250 to 450 °C governing the hot gas cleaning section, the use of e.g. dust settling chambers, cyclones and/or hot electrostatic precipitators is typical for solids removal purposes. At said temperatures, some

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metal compounds, e.g. As_2O_3 , as well as the H_2SO_4 are usually in gaseous form and can thus not be removed by such equipment. Similarly, halides such as chlorides and fluorides will also pass through this equipment. When entering the wet gas cleaning section, the hot gases are quenched with weak acid / water and cooled down adiabatically. Except for the halides, the impurities will condense or sublime and form sub-micron particles which must be removed from the gas by various unit operations.

Halides will usually not condense but remain gaseous, particularly fluorides, and thus must be removed by absorption in suitable aqueous solutions. While absorbed chlorides do typically not express a noticeable vapor pressure, and are hence relatively easy to separate from the gas, absorbed fluorides dissolved in aqueous solution, on the contrary can exert a significant vapor pressure which limits its efficient removal from the gas.

Any impurity slipping through the hot and wet gas cleaning section of the plant will eventually enter the sulfuric acid plant, and will report there to the produced sulfuric acid and hence is regarded as a contaminate for the quality of the product

For metallurgical operations, the gas cleaning and sulfuric acid plant leads to high investment and maintenance costs, but are indispensable based on the need for environmental protection and to avoid pollution. Hence the sulfuric acid is a non-desired by-product which cannot be stored in large quantities and thus must be readily sold or give-away. While good quality acid can be marketed for a reasonable price, lower quality acid, i.e. containing higher amounts of impurities, does attract a significant lower price and is of limited use for e.g. fertilizer production.

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Albeit the recently increasingly higher amount of impurities in the metallurgical off gases, there is simultaneously an increasing demand for better quality product acid and to meet this, the gas cleaning section must be substantially more efficient.

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Sub-micron particles containing substances like arsenic or selenium, H_2SO_4 -mist or metal compounds, can be separated well in scrubbers operating at elevated pressure drop. Downstream wet electrostatic precipitators (wet Electrostatic precipitators) must remove the remainder of those substances from the gas to a degree suitable for the downstream processing of the gas at the sulfuric acid plant.

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All impurities segregated from the gas will eventually transferred and report to the liquors used in the wet gas cleaning section for quenching, scrubbing, cooling. A significant amount of H_2SO_4 is thus contained in said liquors. Eventually a liquor (or a multitude of liquors), usually named weak acid or wash acid, containing all impurities will be discharged from the wet gas cleaning section for further processing at a liquid effluent treatment plant.

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Subject to the chemical activity of the ionic elements in the solution, H_2SO_4 , HCl and H_2F_2 are competing reaction partners and dissolved halides can become less stable (less soluble) at increased H_2SO_4 concentration. Complete absorption of halides is thus getting increasingly difficult with higher H_2SO_4 concentration of the liquid.

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Chlorides are not as critical and usually separated at a gas cooling tower which is required to reduce and meet the desired residual moisture content of the gas. However, the characteristics of the fluorides require specific and additional measures, subject to the level of the fluorides concentration in the incoming gas.

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This invention suggests several highly efficient methods for the removal of fluo-

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rides from metallurgical gases, while minimizing the use of fresh additional process water and hence also minimizing the amount of weak/wash acid discharged from the wet gas cleaning section for downstream liquid effluent treatment.

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A standard specification of technical grade sulfuric acid calls for less than 1 ppm of F, which correlates to less than 1 mg of F per Nm³ of gas leaving the wet gas cleaning section. Premium quality acid requires typically less than 0.2 ppm F. Not only can non-captured fluorides contaminate the product acid, it also renders concentrated acid very corrosive even at the presence of a few ppm, which does seriously affect stainless steel or alloy acid coolers and piping. Fluorides slipping into the acid plant do also attack the glass-fibers of the candle filters at drying and absorption towers. It does also potentially destroy the silica carrier of the V₂O₅ catalyst used for the oxidation of SO₂ to SO₃. So, there are plenty of reasons to control the F-content of the gas leaving the wet gas cleaning section towards the sulfuric acid plant.

However, as pointed out above, the quality of ore is a very fluctuating parameter which is why it is necessary to provide a flexible cleaning system.

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This problem is solved by a claim with the features of claim 1.

Such a process for cleaning SO₂ is directed to a cleaning of a process gas stream containing at least 1.0 wt.-% SO₂. Thereby, the process gas is quenched before it passes a packed bed tower for a further cooling to typically 40°C. Afterwards, the process gas stream is fed into at least one electrostatic precipitator, whereby condensate from the electrostatic precipitator is guided into a water treatment plant.

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This invention is characterized by the separate withdrawal of the condensate of the wet electrostatic precipitators, which contains most of the sulfuric acid entering the wet gas cleaning section. The absence of said sulfuric acid at the other gas cleaning equipment consequently enables the operation there with lower acid concentration and hence a more efficient removal of fluorides there. Eventually this results in savings at process water requirement.

Consequently the sulfuric acid concentrations of the circulating liquors at the gas cooling tower, scrubber and quench remain obviously significantly lower. As a result, the addition of process water can be diminished and thus the amount of liquid effluent is minimized, while still all impurities are discharged. This is based on the improved solubility of fluoride at the gas cooling tower and scrubber circuits.

It is essential that fluoride concentration in the process gas is measured before entering the gas cooling tower and depending on the measured value additional steps can be taken to handle higher fluoride contents as described below.

Depending on the measured value, for fluoride concentrations up to typically 50 mg F/Nm³, water is added in and/or after the gas cooling tower.

Higher fluoride concentration of the process gas (typically 50 – 200 mg F/Nm³) can thus be tolerated. The implementation of the separate discharge of the wet ESP condensate minimizes the addition of process water and subsequently the volume of weak acid to be processed at the liquid effluent treatment plant.

However, overdosing e.g. waterglass can cause gelation, which leads to precipitation and build-ups in acidic environment, thus resulting in plugging of coolers, pipes or packing. This risk is increasing with higher fluoride content. Thus, the minimum but sub-stoichiometric amount must be dosed to meet the limit at the

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gas cooling tower outlet lower of e.g. 1 mg F /Nm³, which can be calculated out of the given operating data. The majority of the fluoride will be absorbed at the gas cooling tower at low acid concentration and low temperature. A smaller fraction is absorbed upstream at the scrubber at higher acid concentration and higher temperature.

Preferably, silicon dioxide (SiO₂), sodium silicate (Na₂SiO₃) and/or potassium silicate (K₂SiO₃) is/are used as reagent, whereby Na₂SO₃ is mostly preferred. This leads to the so-called waterglass-reaction with a stable product, e.g. sodium silicate, which remains in solution.

Even higher fluoride concentrations in process gas (typically 200 to 1000 mg F/Nm³) do require an additional co-current type packed bed fluoride tower to be located between the two stages of wet electrostatic precipitators. Preferably, it is located between the two wet electrostatic precipitators in order to enable operation with lowest presence of H₂SO₄. Additionally or alternatively, liquid from the packed bed tower is partly withdrawn and mixed to the quench stream. Without such additional step, the fluoride concentration at the circulating liquid of the gas cooling tower (even with chemicals dosing) would not allow to achieve the required removal efficiency towards a residual 1 mg F/Nm³ at the gas exit. It was common in the past, that the packing material of this tower is made of silica containing material, which reacts with the fluoride contained in the gas stream and forming soluble H₂SiF₆. This packing has to be renewed or replenished periodically, subject to the fluoride content. Those towers are quite large and massive and thus very costly. It has been observed that the surface of the ceramic packing material was covered with other substances (e.g. soot, lead, hydrocarbons), whereby the silica was thus not accessible anymore to the fluoride, resulting in very low or no effect of such installation.

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As a subject of this invention, it was found, that a separate countercurrent type packed bed fluoride removal tower installed between the both electrostatic precipitators and using plastic packing could handle even very high fluoride containing gas of e.g. in excess of 2000 mg F/Nm³, while maintaining the exit gas quality of < 1 mg F/Nm³ and simultaneously reducing the amount of added chemicals and process water and subsequently also producing less liquid effluent.

At times fluoride peaks may occur. It is then convenient to also have a possibility to add some reaction agent, e.g. Na₂SiO₃, SiO₂, and/or K₂SiO₃ to the gas cooling tower for covering these peaks also. This increases process flexibility further.

Typically, the process gas is used for the production of H₂SO₄ whereby it is possible to produce a saleable product with minimum of impurities.

Since the catalyst used for oxidation of SO₂ to SO₃ is sensible with regard to contained fluoride in the gas, the invention is not only necessary for a constant product quality but also extends operating life of downward process steps.

In a preferred embodiment, the process liquors contains between 1 and 33 wt.-%, preferably 2 and 30 wt.-%, H₂SO₄. This affects the solubility of fluoride which increases the requirements to a flexible fluoride control.

Preferably, a scrubber is foreseen between the quench and the packed bed tower for further cleaning.

In addition or alternatively, condensate from the cooling gas tower and/or the scrubber is used as quench stream in the quench. Thus, liquid effluent streams are minimized.

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The invention also covers a plant for the cleaning of a process gas containing SO₂ with the features of claim 14. Preferably, a process with the feature of any of claims 1 to 13 can be operated in said plant.

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Such a plant comprises at least one quench tower, at least one gas cooling tower and at least one electrostatic precipitator, preferably at least two electrostatic precipitators in series. As the essential part of the invention, condensate from the electrostatic precipitator(s) is withdrawn separately via at least one withdrawing conduit and guided via at least one conduit to a liquid effluent treatment plant.

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Preferably, the plant also contains a pump tank for adding a reaction agent and/or a packed bed tower whereby the packed bed contains silica.

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Summarizing the above, the separate routing of the condensate/drain of the wet ESPs, containing the bulk of the sulfuric acid, directly to the liquid effluent discharge, is key to this invention, - in conjunction with the fluoride tower operation as described above in case of high fluoride intake rates. Thus, the gas cooling tower, scrubber and quench circulations are able to operate at minimized acid content and thus are enabled to better absorb fluorides. As a consequence, the residual fluorides slipping into the fluoride removal tower are therefore minimized and the load on the fluoride tower reduced. Eventually, this also reduces the required amount of waterglass addition.

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This system is based on the separate withdrawal of the wet ESP condensate plus the usage of a certain amount of waterglass. While the bulk of the fluorides are removed upstream of the first step ESP, particularly at the gas cooling tower, only the slippage of fluoride does enter the separate packed bed tower and thus the required reaction agent dosing is only a fraction of the equivalent amount that would be necessary to react with all of the fluoride entering the

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plant. When adding reaction agent up to the equivalent of the stoichiometric demand, the fluoride content of the gas leaving the wet gas cleaning plant can be sustainably kept well below the standard of $< 1 \text{ mg F/Nm}^3$ and hence the production of premium quality sulfuric acid can be ensured.

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All process water required at the wet gas cleaning section is preferably or exclusively added to this fluoride tower, ensuring not only a very weak sulfuric acid concentration there, -usually well below 0.5 wt.-% H_2SO_4 - but also removing the dissolved and stable precipitation product, e.g. Na_2SiF_6 , countercurrent to the gas flow direction towards the quench tower and the liquid effluent treatment plant. Thus, also the risk of overdosing of flocculation agent and hence potential plugging of equipment is eliminated.

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Further features, advantages and possible applications of the invention can be taken from the following description of the drawings and the exemplary embodiments. All features described and/or illustrated form the subject-matter of the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

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20 In the drawings:

Fig. 1 shows a SO_2 cleaning according to the state of the art,

Fig. 2 shows a SO_2 cleaning for relatively low fluoride concentrations according to the invention,

25 Fig. 3 shows a SO_2 cleaning for medium fluoride concentrations according to the invention

Fig. 4 shows a SO_2 cleaning for relatively high fluoride concentrations according to the invention and

Fig. 5 shows a SO_2 cleaning for very high fluoride concentrations according to the invention.

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The standard wet gas cleaning process flow diagram of Fig.1 is characterized by a stepwise countercurrent stream of the aqueous phase (weak acid) to the direction of the gas stream.

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Process gas is fed via conduit 11 into a quench tower 10. Therein, it is quenched with a quench stream fed in via conduit 14. The quench stream is partly circulated via conduit 12, pump 13 and conduit 14. The other part of the quench stream is withdrawn via conduit 15.

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After the quench, the cooled process gas is transported via conduit 16 to a scrubber 20, where it is further cleaned with aqueous sulfuric acid fed in via conduit 23. Parts of the scrubbing liquid is recirculated via conduit 21, pump 22 and conduit 23 and parts are fed into conduit 24 for the quench tower.

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Via conduit 25, the process gas is passed to a gas cooling tower 30 next. Necessary fresh process water is added via a conduit 38 to the gas cooling tower 30. Parts of the liquid in the sump of the gas cooling tower are circulated via conduit 31, pump 32, conduit 33, heat exchanger 34 and conduit 35 while another part is withdrawn via conduit 36. Thereby, the concentration of impurities in the liquid is increasing stage by stage until discharged from the quench tower via conduit 15.

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The cooled process gas is then send to a first electrostatic precipitator 40 and - if wanted - via conduit 41 forward to a second electrostatic precipitator 42. Afterwards, the cleaned sulfur dioxide can be processed further for producing sulfuric acid. Condensate of all electrostatic precipitators 40, 42 are withdrawn via conduits 44, 45 and 46 and passed into the sump of cool gas tower 30, scrubber 20, to the quench tower 10 from where it is discharged in the described way.

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Sulfuric acid in the condensate at the wet electrostatic precipitators 40, 42 has highest concentration of typically 25 - 35% H_2SO_4 , and will be fed upstream to the gas cooling tower circulation with typically only 1 – 10% H_2SO_4 concentration. With higher acid concentrations, the solubility of metal sulfates as well as chlorides, and particularly fluorides is diminishing. To lower the acid concentration and hence also the dissolved fluorides concentration, more process water can be added and thus the removal efficiency of fluorides can be improved. This process is well established at the industry and can successfully operate at feed gas concentrations up to typically 50 mg F/ Nm^3 , while the gas leaving the wet gas cleaning section contains less than 1 mg F/ Nm^3 . Available fresh process water and the capacity of the downstream liquid effluent treatment plant and its investment costs respectively are determining and limiting factors.

The invention is characterized by separately discharging the condensate from the wet Electrostatic precipitators from the wet gas cleaning section and hence a significant amount of sulfuric acid, as sketched in Fig.2.

Condensate of all electrostatic precipitators 40, 42 are withdrawn via conduits 44, 45 and 46 and passed separately to a collection tank 50. From there, it is pumped via pump 52 through conduits 51 and 53 to a liquid effluent treatment plant.

The flow sheet Fig.3 presents an additional dosing of a reaction agent. Said agent is hold available in pump tank 60 from where it is pumped via conduit 61, dosing pump 62 and conduit 63 to the gas cooling tower 30 recirculation, like conduit 35 or into the sump of the gas cooling tower 30.

Fig. 4 shows the used of an additional packed bed tower 70. Thereby, process gas from the first electrostatic precipitator 40 is fed into this additional packed

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bed tower 70. The packing material of this packed bed tower 70 is made of silica containing material, which reacts with the fluoride contained in the gas stream and forming soluble H_2SiF_6 .

- 5 Via conduit 77, fresh water is injected into the packed bed tower 70. Parts of liquid is recirculated from the sump of the packed bed tower 70 via conduit 72, pump 73 and conduit 74 to the top of the packed bed tower 70 while another part is withdrawn via conduit 76 and passed to the gas cooling tower 30.
- 10 Another flow sheet in the sense of the invention is depicted in Fig.5. In contrast to figure 4, an additional conduit 66 is foreseen. Via that conduit 66, it is possible to feed additional reaction agent from pump tank 60 into the packed bed tower 70 to catch so peaks in the process gas' fluoride concentration.

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List of Reference Numerals:

	10	quench tower
5	11,12	conduit
	13	pump
	14-16	conduit
	20	scrubber
	21	conduit
10	22	pump
	23-25	conduit
	30	Gas cooling tower
	31	conduit
	32	pump
15	33	conduit
	34	heat exchanger
	35-39	conduit
	40	electrostatic precipitator
	41	conduit
20	42	electrostatic precipitator
	43-46	conduit
	50	pump tank
	51	conduit
	52	pump
25	53	conduit
	60	pump tank
	61	conduit
	62	dosing pump
	63	conduit
30	70	packed bed tower

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71,72	conduit
73	pump
74-77	conduit

Claims

1. Process for cleaning SO₂, wherein a process gas stream containing at least 1.0 wt.-% SO₂, wherein the feed is quenched prior to passing into a packed bed tower and is then fed into at least one electrostatic precipitators, **characterized in** that whereby condensate from the at least one electrostatic precipitator is separately withdrawn and guided into a effluent water treatment plant.
2. The process according to claim 1, **characterized in** that the fluoride concentration in the process gas is measured before leaving the electrostatic precipitator and depending on the measured value the following steps are taken:
 - (i) for fluoride concentrations below 50 mg F/Nm³, process water is added to the system to improve the solubility of the F in the liquor and/or
 - (ii) for fluoride concentrations between 50 and 250 mg F/Nm³ a reaction agent is added in and/or after the gas cooling tower and/or
 - (iii) for fluoride concentrations between 200 and 1000 mg F/Nm³ the process gas stream is guided after the first electrostatic precipitator through a packed bed tower wherein the packed bed is made of silica containing material.
3. The process according to claim 1 or 2, **characterized in** that continuously measured values of the F-concentration in the gas are used for controlling and/or adjustment of the amount of reaction agent fed to the gas cooling tower and/or the fluoride removal tower.

4. The process according to claim 2 or 3, **characterized in** that SiO_2 , Na_2SiO_3 and/or K_2SO_3 is used as reaction agent, added to a co-current packed bed tower.
- 5 5. The process according to any of claims 2 or 4, **characterized in** that the packed bed fluoride removal tower is foreseen between two electrostatic precipitator steps.
- 10 6. The process according to any of claims 2 to 5, **characterized in** that reaction agent can be added to the packed bed fluoride removal tower.
- 15 7. The process according to claim any one of the preceding claims, **characterized in** that the process gas is used for production of H_2SO_4 .
8. The process according to any one of the preceding claims, **characterized in** that the process gas is off-gas of a metallurgical process.
- 20 9. The process according to any one of the preceding claims, **characterized in** that the process gas is fed to the quench at temperatures between 250 and 450 °C.
- 25 10. The process according to any one of the preceding claims, **characterized in** that in the quench the circulating liquor contains between 1 and 35 wt.-% H_2SO_4 .
- 30 11. The process according to any one of the preceding claims, **characterized in** that in the process gas is quenched to a temperature between 50 and 90 °C.

12. The process according to any one of the preceding claims, **characterized in** that a scrubber is foreseen between the quench and the packed bed tower.
- 5 13. The process according to any one of the preceding claims, **characterized in** that condensate from the packed bed tower is added to the circulating liquor stream in the quench.
- 10 14. Plant for cleaning SO₂ containing gas, according to any one of the preceding claims, comprising at least one quench tower (10), at least on gas cooling tower (30) and at least on electrostatic precipitator (40,42), **characterized in** that at least on conduit (43,44,45) is foreseen to withdraw the liquid phase from the electrostatic precipitator(s) (40,42) and passing it to a liquid effluent treatment plant.

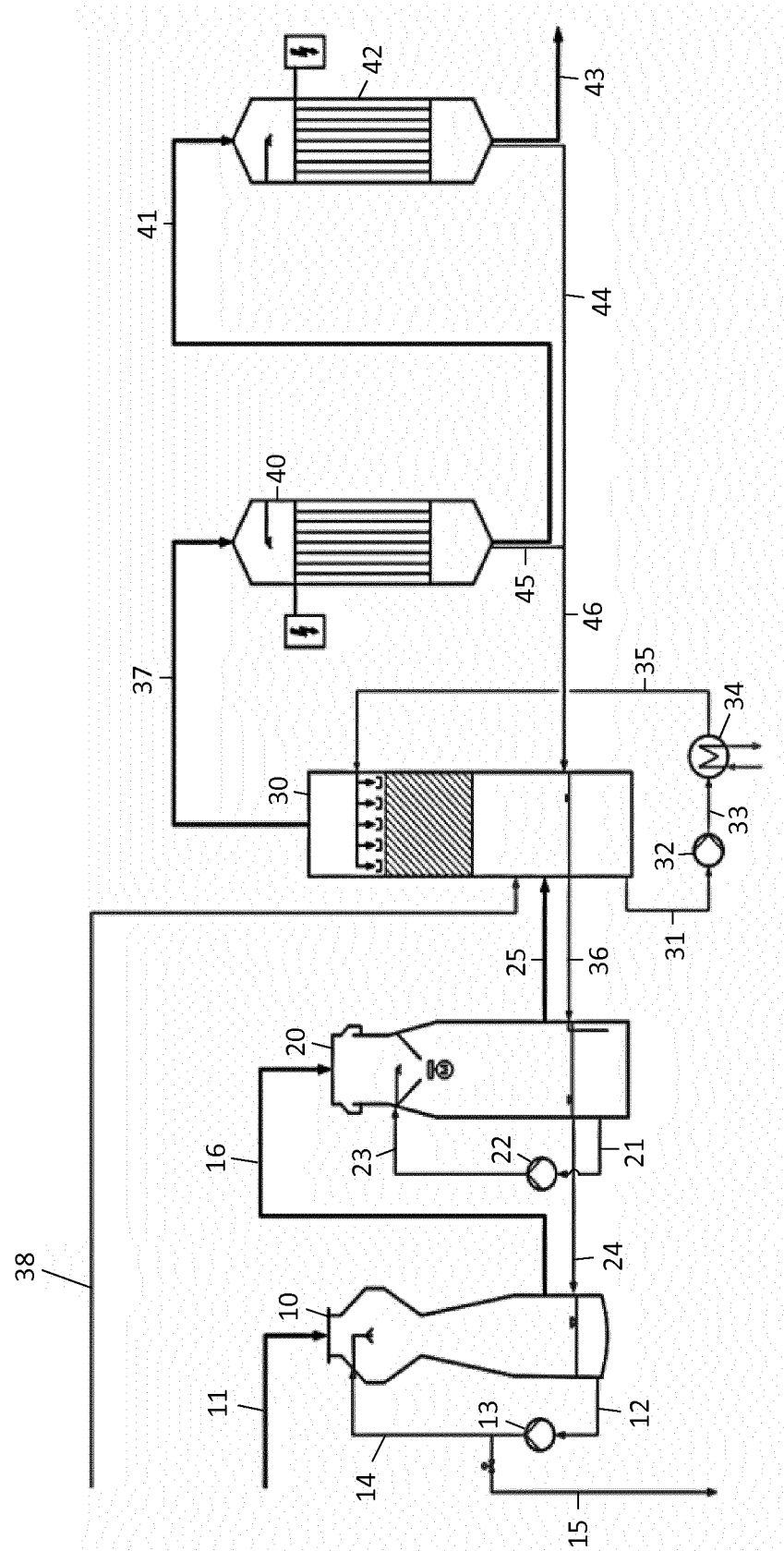


Fig. 1

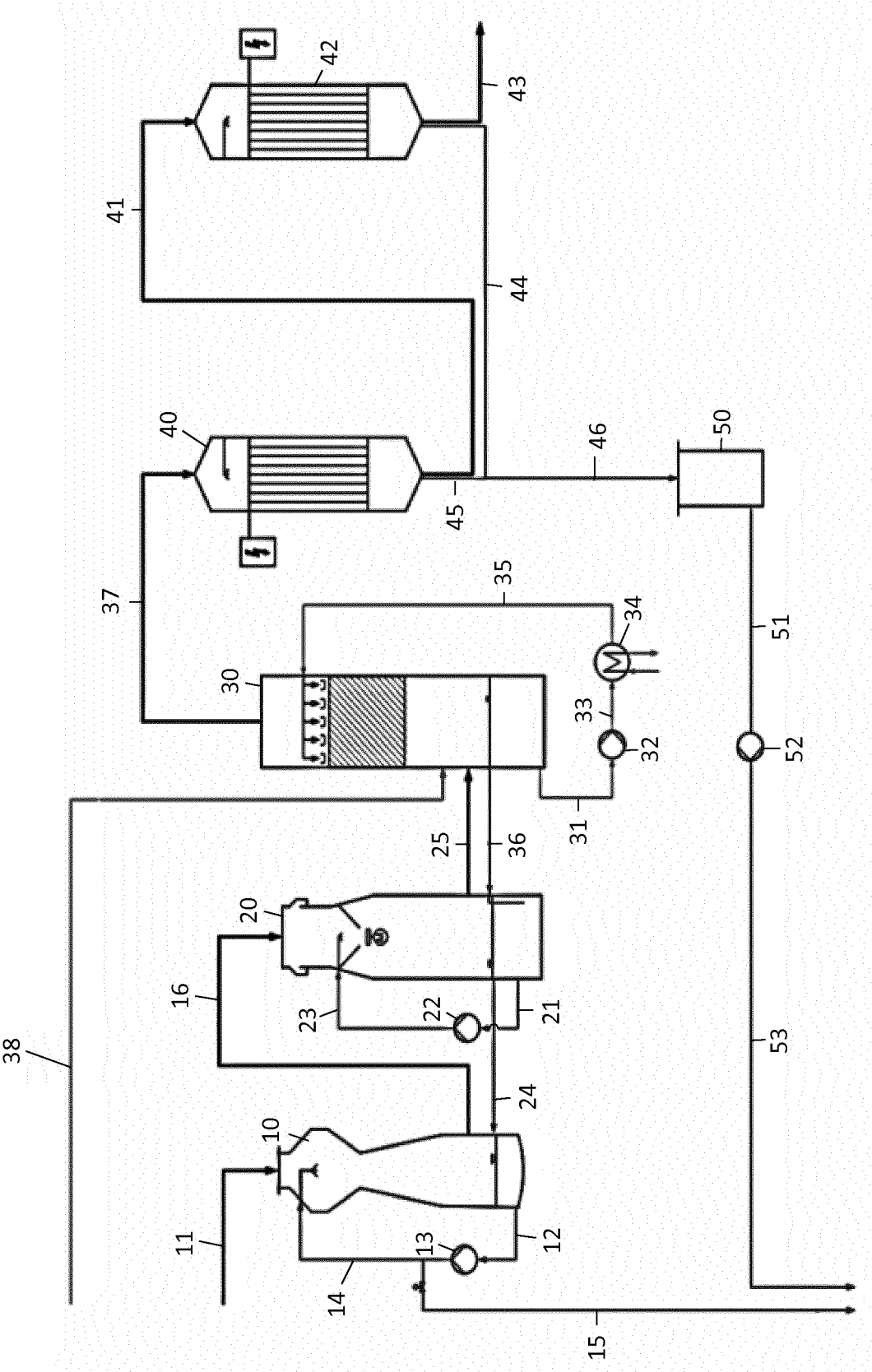


Fig. 2

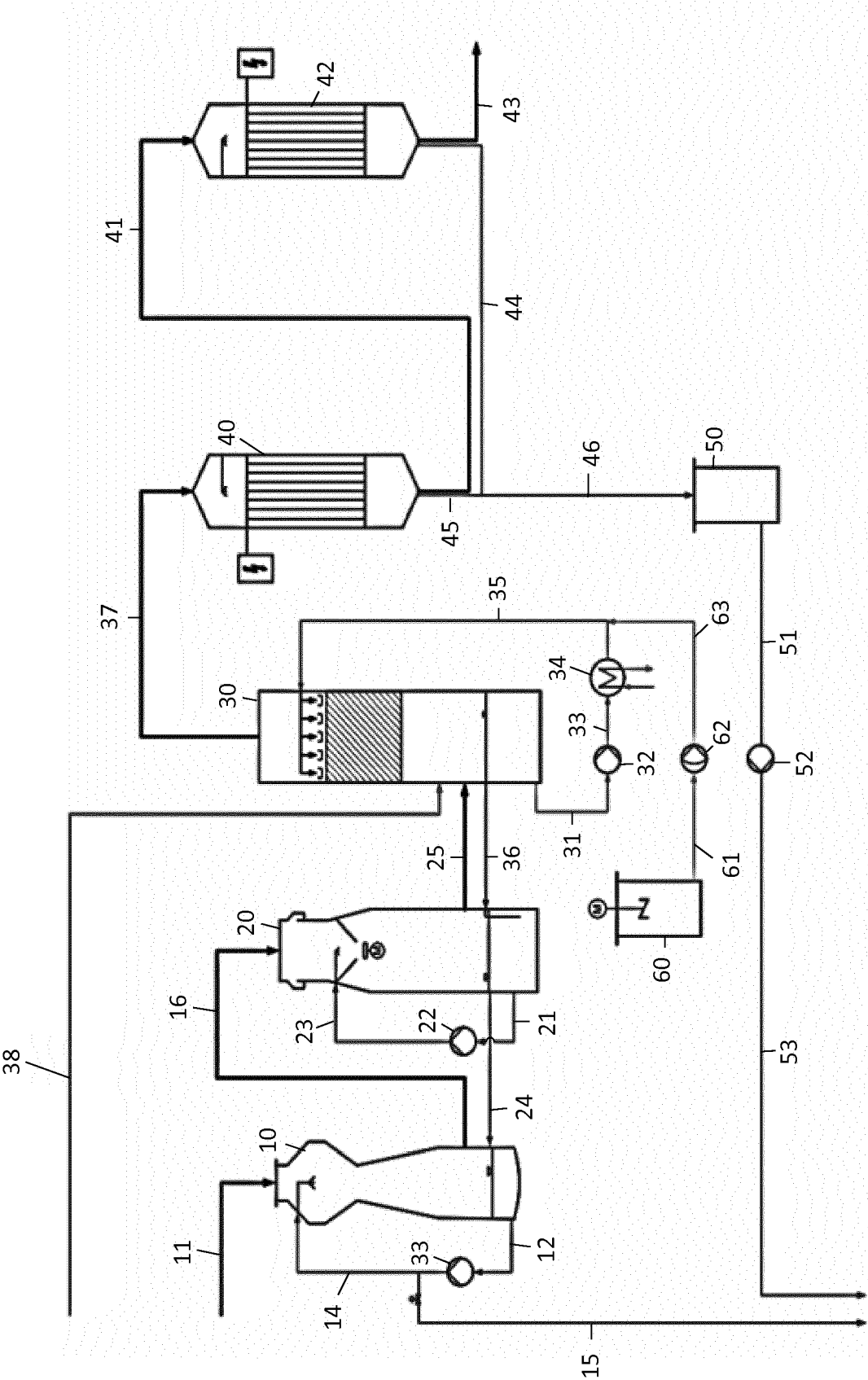


Fig. 3

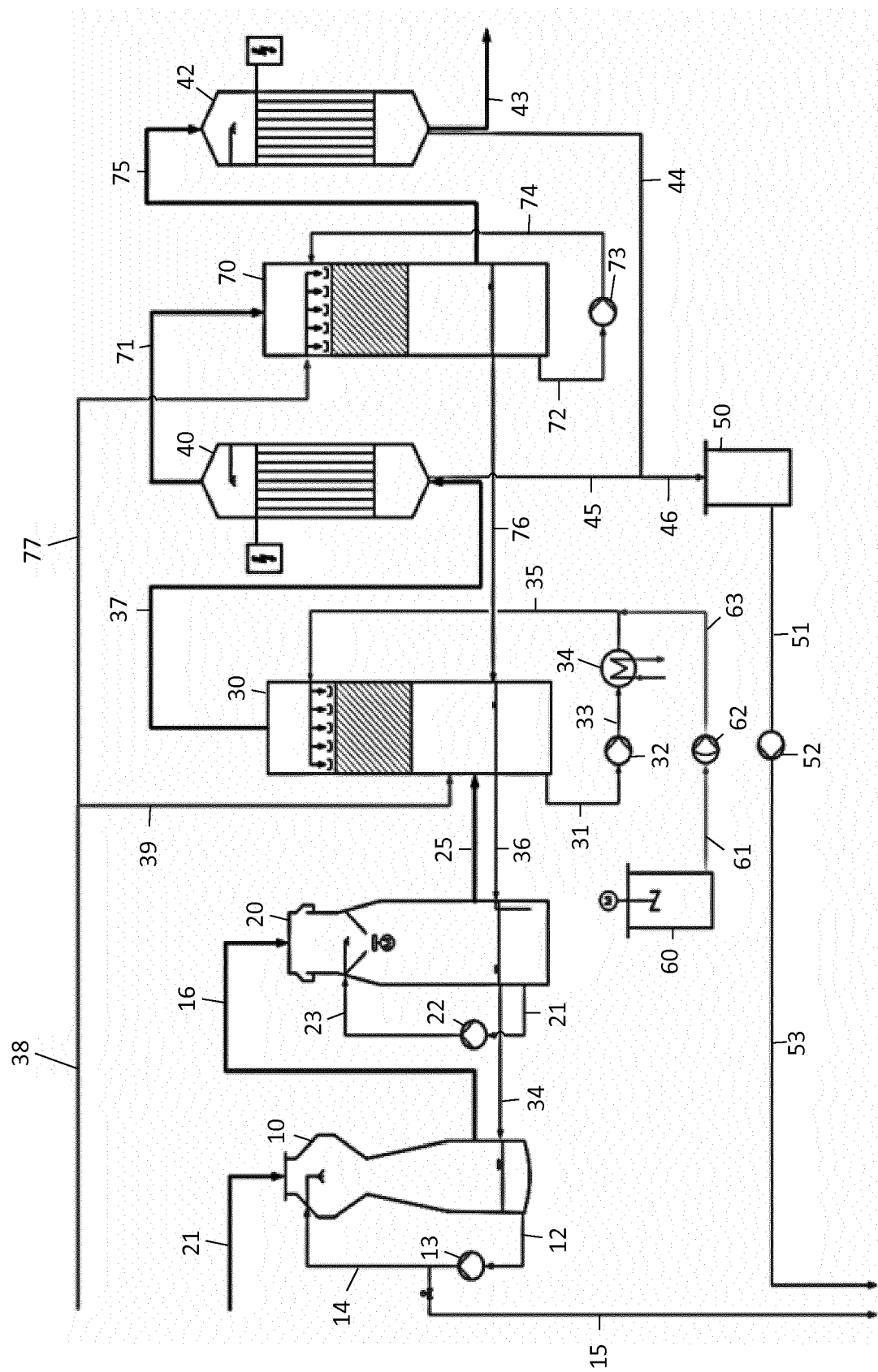


Fig. 4

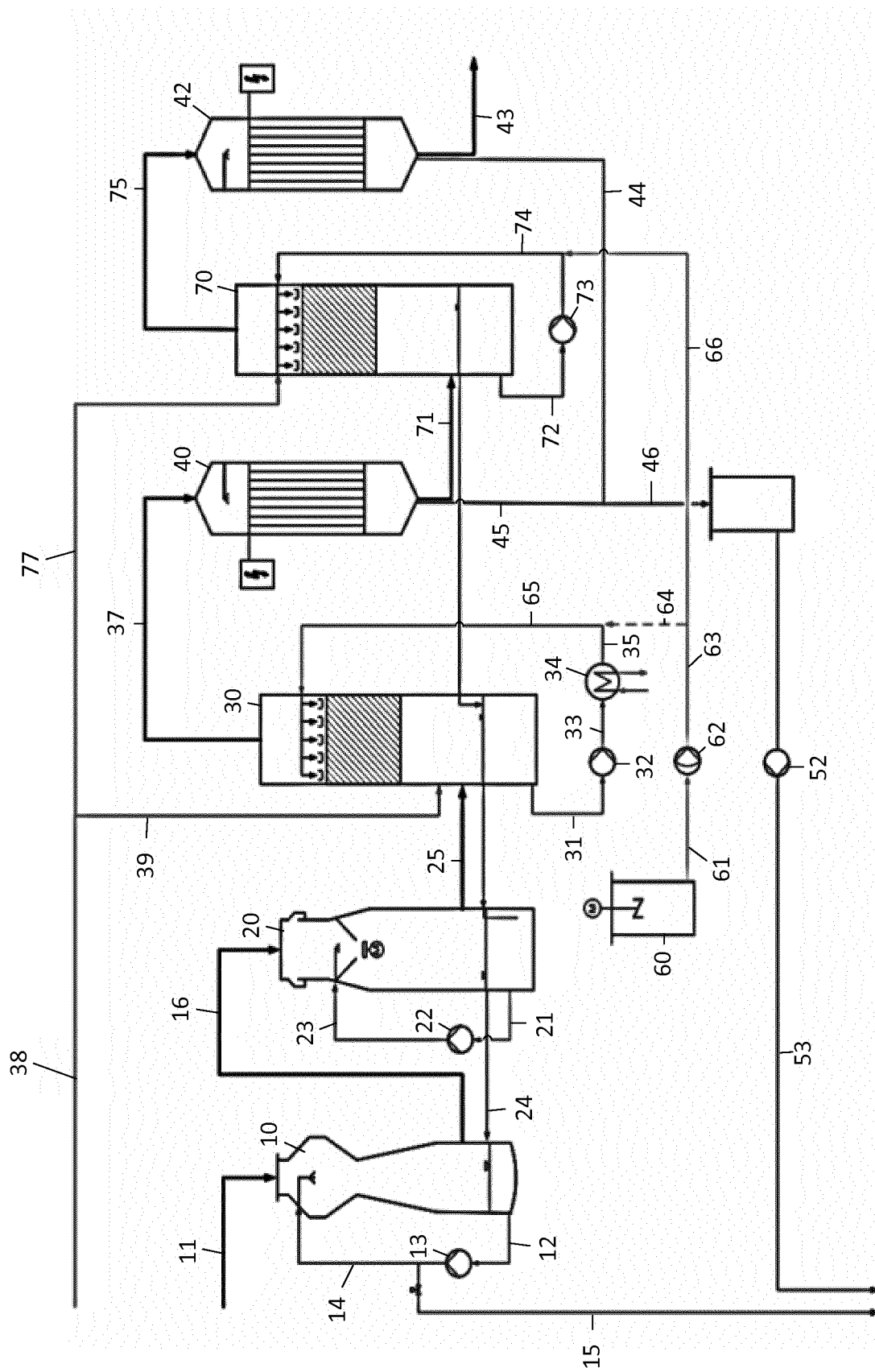


Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/050318

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01D53/32	B01D53/68
		B01D53/75
		C01B17/56
		B01D53/78
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)		
B01D C01B		
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		
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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Y	column 1, line 1 - column 1, line 12 column 2, line 42 - column 2, line 64; figure 1	1-14
Y	----- EP 0 808 660 A1 (MITSUBISHI HEAVY IND LTD [JP]) 26 November 1997 (1997-11-26) figures 8,9	1-14
X	----- EP 0 101 780 A1 (PETERSEN HUGO VERFAHRENSTECH [DE]) 7 March 1984 (1984-03-07)	1-14
Y	page 1, line 1 - page 2, line 7; claims 1-3; figures 1-3	1-14
	----- -/-	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
27 September 2018		11/10/2018
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer de Biasio, Arnaldo

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Information on patent family members

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