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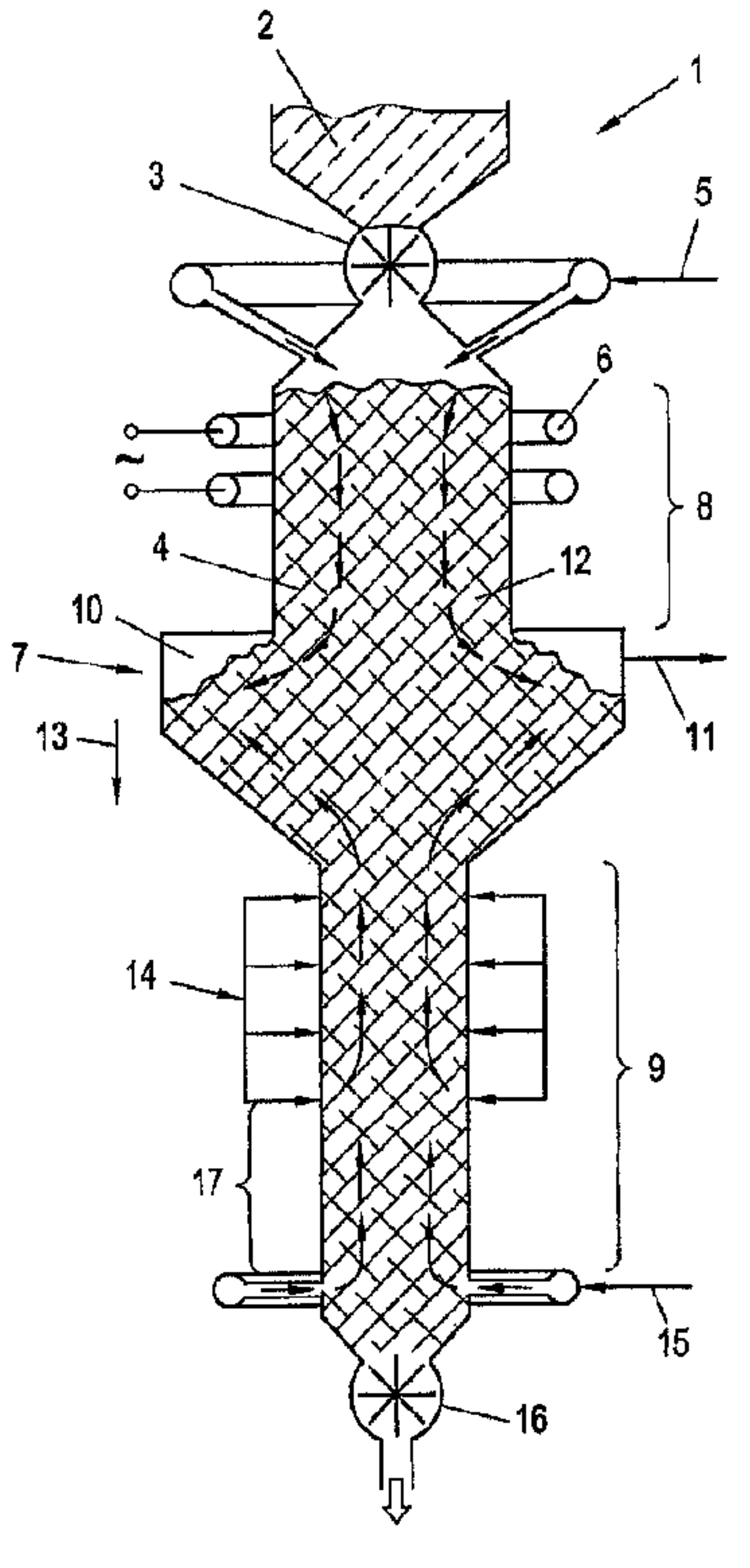
(72) **Inventeurs/Inventors**:
EDLINGER, ALFRED, AT;
DAIMER, JOHANN, DE

(73) **Propriétaire/Owner**:
SGL CARBON SE, DE

(74) **Agent**: FETHERSTONHAUGH & CO.

(54) **Titre** : PROCEDE POUR TRAITER DU MATERIAU CATHODIQUE USAGE CONTENANT DU CARBONE
(54) **Title**: METHOD FOR PROCESSING USED CARBON-CONTAINING CATHODE MATERIAL



(57) **Abrégé/Abstract**:

In a method for processing used cathode material containing carbon, in particular used cathode troughs from aluminum production, wherein the cathode material is put into a shaft furnace and, in order to gasify carbon, is subjected to a thermal treatment in the shaft furnace at a temperature above the ignition temperature of the carbon and above the evaporation temperature of toxic substances contained in the used cathode material, the reaction gases are conducted cocurrent with the carbon in a first longitudinal section of the shaft furnace and countercurrent to the carbon in a second longitudinal section of the shaft furnace, wherein the reaction gases are drawn from a region of the shaft furnace having an enlarged cross-section between said longitudinal sections and are preferably subjected to an aftertreatment.

Abstract

In a method for processing used cathode material containing carbon, in particular used cathode troughs from aluminum production, wherein the cathode material is put into a shaft furnace and, in order to gasify carbon, is subjected to a thermal treatment in the shaft furnace at a temperature above the ignition temperature of the carbon and above the evaporation temperature of toxic substances contained in the used cathode material, the reaction gases are conducted cocurrent with the carbon in a first longitudinal section of the shaft furnace and countercurrent to the carbon in a second longitudinal section of the shaft furnace, wherein the reaction gases are drawn from a region of the shaft furnace having an enlarged cross-section between said longitudinal sections and are preferably subjected to an aftertreatment.

Method for Processing Used Carbon-Containing Cathode Material

The invention relates to a method for processing used carbon-containing cathode material, in particular used cathode troughs from aluminum production, in which the cathode material is placed in a shaft furnace and, in order to gasify carbon, is subjected to a thermal treatment in the shaft furnace at a temperature above the ignition temperature of the carbon and above the evaporation temperature of toxic substances contained in the used cathode material.

In aluminum production according to the Hall-Heroult process, aluminum oxide is reduced during molten mass electrolysis. The electrolysis cell most often consists of a steel trough clad with carbon material (graphite/anthracite) and a refractory material, such as fireclay. The carbon cladding serves as the cathode during electrolysis, and as such will subsequently be referred to as a cathode trough. Used cathode troughs, also called spent potliners, accumulate in large quantities during aluminum production according to the Hall-Heroult process, and have always posed problems relating to disposal due to their high content of toxic substances. The toxic substances include cyanide, which forms out of the carbon in the cathode troughs and nitrogen in the air, and various metal fluorides, such as sodium and aluminum fluoride, which are formed out of the metal species contained in the bauxite in conjunction with the fluoride of the cryolite used in the Hall-Heroult process. When changing out the used cathode troughs, the latter are removed from the electrolysis cell together with a refractory encircling wall, so that the spent potliners cleaned in this way predominantly still contain aluminum, silicon, calcium and magnesium oxide from the refractory material.

For example, a method of the kind mentioned at the outset became known from Canadian Patent Application CA 2 308 545 A1. In this method, used cathode troughs from aluminum production are gassed in a shaft furnace, and the formed reaction gasses are removed. However, the disadvantage to the process according to this prior art is that the alkali metals also contained in the used cathode troughs tend to form circuits in such shaft furnaces, thereby becoming concentrated in the shaft furnace, and leading to accretions and slopes in conjunction with elevated refractory wear and dust emission, and to a diminished quality for potentially formed slag from the starting materials.

Therefore, the object of the present invention is to indicate an improved method with which the mentioned toxic substances can be completely separated and obtained from the used cathode material, while at the same time preventing the formation of alkali circuits.

In order to achieve this object, the method mentioned at the outset is developed further according to the invention so that the reaction gases are conducted co-currently with the carbon in a first longitudinal section of the shaft furnace, and counter-currently to the carbon in a second longitudinal section of the shaft furnace, and that the reaction gases are drawn from a region of the shaft furnace having an enlarged cross section, in particular an enlarged diameter, between the specified longitudinal sections, and preferably subjected to an aftertreatment. Because the reaction gases are drawn in a central area along the longitudinal axis of the shaft furnace (central gas vent), alkali circuits are interrupted, and the reaction gases containing the mentioned toxic substances in the form of sodium fluoride (NaF), aluminum fluoride (AlF_3), hydrofluoric acid (HF), nitrogen (N_2) and potentially additional alkaline and alkaline earth fluorides in addition to synthesis gas (CO + H_2) can be relayed to further reprocessing.

The process itself takes place autothermally due to the high C content once the carbon has reached the ignition temperature and enough oxygen is available for gassing purposes. However, in order to initiate the process or provide support during the process, another embodiment envisages that the furnace be heated to heat the carbon of the used cathode material to the reaction temperature. This heating can basically be conducted in any of the ways known to the expert. In one embodiment, for example, the energy for thermal treatment can be introduced into the carbon to be reprocessed via electric induction. In this case, induction coils can be arranged around the periphery of the shaft furnace in the area of the dispensing end of the shaft furnace, and used to build up an induction field to which the introduced carbon of the used cathode material becomes coupled, and thereby heated. According to an alternative embodiment to the above, heating can also be accomplished through fossil firing, for example by positioning a combustion chamber in the shaft furnace, preferably in the first longitudinal section of the shaft furnace, and in particular in the upper region of the first longitudinal section, by means of which the shaft furnace has introduced into it a fuel, such as natural gas, petroleum, coal dust, dust generated by used cathode troughs or the like, optionally mixed in with an oxidation gas, such as oxygen or air. In another variant of this embodiment, a supply line that empties into the first longitudinal section of the shaft furnace, preferably into the upper region of the first longitudinal section of the shaft furnace, can be provided, through which the shaft furnace is supplied with fuel, optionally mixed in with oxidation gas. In another variant of this embodiment, the first longitudinal section of the shaft furnace, preferably the upper region of the first longitudinal section of the shaft furnace, can incorporate one or more lances that preferably extend essentially in the direction of the longitudinal extension of the shaft furnace, through which the shaft furnace is supplied with fuel and oxidation gas, either separately or mixed together. As an alternative to heating via induction or fossil firing, the carbon of the used carbon-containing cathode material can also be brought to the reaction temperature by placing a partial quantity of already incandescent coke or graphite on the used cathode material introduced into the shaft furnace, or by adding a partial quantity of already incandescent coke or graphite to the used cathode material during or before its introduction into the shaft furnace.

The present invention is basically not limited with respect to either the absolute or relative dimensions of the individual longitudinal sections. However, especially good results are obtained when the length of the first longitudinal section measures 40 to 80%, preferably 50 to 70%, and especially preferably 60 to 70% of the overall length of the shaft furnace.

A further development of the inventive idea proposes that the length of the second longitudinal section preferably measure 20 to 60%, especially preferably 30 to 50%, and eminently preferably 30 to 40% of the overall length of the shaft furnace.

The shaft furnace or its longitudinal sections can here exhibit a circular cross section. However, a rectangular cross section is preferred for inductively heated shaft furnaces. This is preferred in particular in light of the skin effect, which ends up limiting the penetration depth of the electrodynamic field.

In order to maintain the carbonization of the carbon, a preferred embodiment of the present invention provides that oxygen be blown into the first and/or second longitudinal section of the shaft furnace. In regions where the oxygen hits the carbon heated at least to ignition temperature, the carbon is oxidized to CO_2, but the latter is again reduced to CO in the carbon fill in the shaft furnace, thereby satisfying Boudouard's equilibrium. As a result, the carbon is not completely burned, but merely gassed, so that carbon monoxide with a calorific value can be obtained. Under the prevailing reaction conditions, the cyanide (CN^- compound) contained in the used cathode material is also converted into carbon monoxide and nitrogen, and thereby completely destroyed.

In order to separate out alkali metals, their compounds and fluoride, the method according to the invention is preferably further developed in such a way that water or steam is blown into the first and/or second longitudinal section of the shaft furnace. Fluorides and alkali compounds, for example those present as sodium fluoride, are volatilized in the presence of water or steam according to the following reaction scheme, and thereby converted into the gaseous phase:

$$2NaF + H_2O \rightarrow Na_2O + 2HF$$
$$Na_2O + C \rightarrow 2Na + CO$$
$$Na_2O + CO \rightarrow 2Na + CO_2$$

Elementary sodium is gaseous, and is removed via the central gas vent, before condensation on colder filling material wandering downward through the furnace causes circuits to form in the shaft furnace. In the gaseous phase, which also contains hydrofluoric acid (HF), sodium fluoride is again formed, and can be separated out during the ensuing waste gas treatment.

Another option for removing fluorides is to react them with silicon dioxide as follows:

$$SiO_2 + 4NaF \rightarrow SiF_4 + 2Na_2O.$$

In a preferred embodiment, the method according to the invention is implemented in such a way as to blow oxygen and water or steam into the shaft furnace by means of lances. This measure deals with a problem where, when oxygen or water/steam are only blown in through nozzles that empty at the wall of the shaft furnace, just the border areas of the shaft furnace or the carbon fill in the shaft furnace are supplied, while the interior region of the carbon fill cross section remains undersupplied, as a result of which the reaction rate is very low in these areas, or it might be impossible to achieve an autothermal process at all. By introducing oxygen and water/steam with the help of lances, the mentioned substances can be introduced precisely to those locations lying in the area of inductive heating, thereby generating reaction spaces that are hot enough for the process to subsequently run its course autothermally along the entire shaft furnace. At this juncture, it is also possible to blow in powdery or dusty used carbon-containing cathode material, in particular cathode troughs.

If the carbon of the used cathode material is not completely gassed in the shaft furnace, the method can preferably be developed further by dissolving the non-gassed carbon in an iron bath. The iron bath can here be inductively heated, for example. The iron bath ensures outstanding dissolution kinetics for carbon, and is easy to regenerate by blowing in oxygen, so-called refining. Since this refining is an exothermal reaction, the thermal balance of the method is improved in this way. The oxygen can also be blown in continuously, so as to keep the iron bath constantly C-undersaturated.

In a further development of the inventive idea, it is proposed within the framework of an especially preferred embodiment of the present invention that an additive be incorporated into the used carbon-containing cathode material during or before its introduction into the shaft furnace in order to slag refractory material, i.e., as described above, in particular aluminum, silicon and magnesium oxide, which are present in the used carbon-containing cathode material as residues of the refractory lining. Possible additives include elementary calcium and all calcium-containing compounds, which are also referred to below as Ca carriers, elementary magnesium as well as all magnesium-containing compounds, which are also referred to below as Mg carriers. Examples of suitable Ca carriers are CaO and $CaCO_3$, e.g., which are available in the form of steel mill slag, limestone or anhydrous lime, and preferably introduced into the process in coarse pieces to ensure that the carbon fill or column can always be thoroughly gassed. Examples of suitable Mg carriers are MgO and $MgCO_3$, which are also preferably introduced into the process in coarse pieces to ensure that the carbon fill or column can always be thoroughly gassed. In this embodiment, the reaction between the additive, i.e., preferably the Ca carrier or Mg carrier, and the aluminum, silicon and magnesium oxides of the refractory material can yield high quality slag, specifically, when adding Ca carriers, high quality calcium aluminate slag, which exhibit outstanding hydraulic properties, and can thus be advantageously used in the cement industry for manufacturing hydraulic binders. The addition of Mg carriers produces high quality magnesium aluminate slag or spinel slag, for example which can be used as refractory concrete.

In the aforementioned embodiment, as much Ca carrier and especially preferably calcium oxide is added to the used carbon-containing cathode material during or before its introduction into the shaft furnace to ensure that a calcium aluminate slag with an Al_2O_3 content of 50 to 70%, preferably 55 to 65 %w/w, and especially preferably about 60 %w/w, is generated in the shaft furnace. A melt phase here arises at under 1600°C. As an alternative thereto, it is equally preferred that as much Ca carrier and especially preferably calcium oxide be added to the used carbon-containing cathode material during or before its introduction into the shaft furnace to ensure that a calcium aluminate slag with an Al_2O_3 content of more than 70 to 90 %w/w, preferably 75 to 85 %w/w, and especially preferably about 80 %w/w, is generated in the shaft furnace. The high melting point of the slag here gives rise to a sintering phase. In light of their composition and quality, these calcium aluminates are suited in particular for use in generating quick cements, increasing the early strength of composite elements, or in the form of sulfate-induced slag cements or gypsum-slag cements. Therefore, the use of these calcium aluminates in cements is especially advantageous, since it enables a significant reduction in the clinker factor during cement production, i.e., in the percentage of Portland cement clinkers per ton of cement. This is advantageous in terms of climate policy, because roughly 1 ton of carbon dioxide is produced during the manufacture of 1 ton of Portland cement clinkers. Furthermore, the calcium aluminates fabricated in this way can be used for manufacturing refractory materials and manufacturing 1/3 slag, i.e., a mixture comprised of CaF_2, Al_2O_3 and CaO, which in turn is employed for obtaining heavy-duty steel components. Aside from the above, the calcium aluminates fabricated in this way can also be used in the area of pig iron desulphurization or secondary metallurgy, which is also advantageous among other things since it avoids the problematic use of calcium fluoride.

The method according to the invention preferably employs used carbon-containing cathode material with an aluminum oxide content of 10 to 45%, especially preferably of 15 to 30%.

The aforementioned embodiment, in which an additive is incorporated into the used carbon-containing cathode material during or before its introduction into the shaft furnace, can also be combined with the embodiment in which the carbon of the used carbon-containing cathode material is not completely gassed, and the carbon that was not gassed is dissolved in an iron bath.

However, as an alternative to executing the process with an iron bath, the method can also be implemented in such a way according to another preferred embodiment as to completely gas the carbon in the cathode material and remove the remaining calcinate. In this case as well, an additive, especially preferably a Ca carrier and/or Mg carrier, can, but does not have to, be incorporated in the used carbon-containing cathode material during or before its introduction into the shaft furnace. If no additive is incorporated, a dry, practically carbon-free calcinate made up of aluminum and silicon oxide is discharged, which can also find application in the cement industry.

It was observed that incomplete calcinate can disintegrate into carbon-containing powder. However, in light of the powder form, the latter is then no longer permeable to gas, and the corresponding shaft furnace section can no longer be thoroughly gassed. The following aftertreatment options are conceivable. Aftertreatment can take place in the iron bath as described above. Alternatively, the powder can be treated with steam for decarbonization purposes, as a result of which a simultaneous cooling is achieved due to the endothermic, heterogeneous water-gas reaction.

As already indicated further above, elementary sodium along with sodium oxide (Na_2O) recombines in the gaseous phase in the presence of hydrofluoric acid (HF) to sodium fluoride (NaF). For sodium oxide, the reaction equation is to be written out as follows:

$$Na_2O + 2HF \rightarrow 2NaF + H_2O$$

For the gaseous sodium, the reaction equation must here be written out as follows:

$$Na + HF \rightarrow NaF + \frac{1}{2} H_2$$

The following secondary reaction can be observed:

$$2Na + H_2O \rightarrow Na_2O + H_2$$

If the objective is now to obtain problematic, but economically interesting hydrofluoric acid in the gaseous phase, the method is preferably implemented using a strongly acidic slag. Given the presence of a strongly acidic slag, wherein the acid component can be formed by silicon oxide and/or aluminum oxide, for example, hydrofluoric acid is regenerated according to the following reaction equation:

$$2NaF + SiO_2 + H_2O \rightarrow Na_2SiO_3 + 2HF$$

or

$$NaF + Al_2O_3 + H_2O \rightarrow NaAl_2O_4 + HF$$

In order to control the products obtained in the gaseous phase as respectively desired, the method is thus preferably further developed in such a way that the basicity in the shaft furnace can be adjusted by adding basic or acidic ingredients, in particular CaO or SiO_2.

An especially preferred process provides for the alternating addition of basic and acidic ingredients. In this way, sodium fluoride and hydrofluoric acid are alternately obtained. The hydrofluoric acid can be reacted with alumina (Al_2O_3) to form aluminum fluoride (AlF_3) and water, wherein the aluminum fluoride can be further processed with the sodium fluoride (NaF) obtained during the basic process to form cryrolite (Na_3AlF_6), which in turn can be used in aluminum production according to the Hall-Heroult process.

$$12NaF + 4AlF_3 \rightarrow 4Na_3AlF_6$$

If the load of toxic substances, such as cyanides, alkali metals and their fluorides, is too high, it may happen that the carbon of the used cathode material will not be coupled through electric induction when exposed to heating as described above. In this case, it is preferred that the method according to the invention be further developed in such a way as to also introduce unused graphite or coke to the carbon of the used cathode material. At a suitable frequency, the unused carbon is coupled to the induction field and heats up, wherein the actual carbon to be reprocessed is also brought to temperature through contact with the incandescent graphite or coke.

The method is preferably implemented in such a way that the reaction gases are drawn at a temperature of 800°C to 1200°C, in particular 900°C to 1100°C, especially 1000°C, and relayed to aftertreatment, thereby preventing a condensation of reaction gases or toxic substances in the line systems, and ensuring a controlled waste gas treatment.

The maximum temperature in the furnace hearth here preferably measures 1200 to 1700°C, especially preferably 1400 to 1700°C, and eminently preferably 1500 to 1600°C. This maximum temperature is diminished up to the central gas vent by endothermic reactions and heat losses to a maximum of 1200°C.

In a further development of the inventive idea, it is proposed that the aftertreatment of the reaction gas drawn from the shaft furnace take the form of a waste gas treatment free of wastewater. For example, this can take place by routing reaction gas drawn from the shaft furnace, which aside from carbon monoxide, carbon dioxide, hydrogen, possibly water, and dust discharged from the reactor, also contains volatilized compounds, including in particular hydrofluoric acid, sodium fluoride, aluminum fluoride and others, into a cooled and preferably isothermally operated fluidized bed reactor, which contains particles comprised of aluminum oxide, sodium fluoride, aluminum fluoride, calcium carbonate, aluminum hydroxide or the like. The temperature of the fluidized bed can here be easily set to a suitable value, for example by means of a water-powered heat exchanger or a water evaporator, wherein the strong turbulence of the fluidized bed ensures a uniform temperature in the shaft furnace, for example of about 1000°C, about 1100°C or about 1200°C. The volatilized compounds of the waste gas are quickly cooled, condensed and possibly reacted on the fluidized aluminum oxide particles, as a result of which cryolite or similar compounds form on the aluminum oxide particles. Waste gas cleaned in this way is drawn from the fluidized bed reactor, wherein any remaining aluminum oxide particles loaded with reaction products are separated out of the waste gas in a cyclone situated downstream from the reactor, or in another dry absorption process on alumina or aluminum oxide in a counter-current at a low temperature. Silicon fluoride (SiF_4) can optionally also be separated out of the waste gas obtained in this way. Aside from being free of waste water, this aftertreatment has the advantage of requiring only comparatively small devices. Another advantage to this aftertreatment is that heat is generated in the process, which can be used to heat up the process steam required for the shaft furnace. In addition, the product comprised of the particles and waste gas can be used in aluminum production.

According to one aspect of the present invention, there is provided a method for processing spent carbon-containing cathode material, in particular spent pot liners from the production of aluminium, in which the cathode material is placed in a shaft furnace and undergoes a heat treatment in order to gasify carbon at a temperature above the ignition temperature of the carbon and above the vaporization temperature of toxic substances contained in the spent cathode material, wherein in a first longitudinal section of the shaft furnace, the reaction gases are conveyed as a co-current with the carbon and in a second longitudinal section of the shaft furnace, the reaction gases are conveyed as a counter-current to the carbon and in that the reaction gases are withdrawn from a region of the shaft furnace with an enlarged cross section between said longitudinal sections.

The present invention will be described below strictly by way of example based on advantageous embodiments, with reference to the attached drawings.

Shown on:

Fig. 1	is a schematic view of a shaft furnace suitable for implementing the method according to the invention based on a first exemplary embodiment;
Fig. 2	is a schematic view of a shaft furnace with an iron bath suitable for implementing the method according to the invention based on another exemplary embodiment;

Fig. 3	is a schematic view of a shaft furnace with an iron bath suitable for implementing the method according to the invention based on yet another exemplary embodiment;
Fig. 4	is a schematic view of an overall system suitable for implementing the method according to the invention;
Fig. 5	is a schematic view of a shaft furnace suitable for implementing the method according to the invention based on another exemplary embodiment;
Fig. 6	is a schematic view of a shaft furnace suitable for implementing the method according to the invention based on yet another exemplary embodiment;

Fig. 7	is a schematic view of the upper partial piece of a shaft furnace suitable for implementing the method according to the invention with fossil heating based on another exemplary embodiment;
Fig. 8	is a schematic view of the upper partial piece of a shaft furnace suitable for implementing the method according to the invention with fossil heating based on another exemplary embodiment;
Fig. 9	is a schematic view of the upper partial piece of a shaft furnace suitable for implementing the method according to the invention with fossil heating based on another exemplary embodiment.

A shaft furnace is marked 1 on Fig. 1, and while implementing the method according to the invention at position 2, has placed in it used, crushed cathode troughs, which are also referred to as spent potliners. The carbon pieces are brought into the shaft 4 of the shaft furnace 1 by means of a rotary valve 3, wherein oxygen can already be introduced up to the height of the rotary valve 3 via a ring line 5. Induction loops marked 6 are used to introduce an induction field in the cross section of the shaft furnace 1, so that the carbon of the used cathode troughs is coupled, and heated up to an ignition temperature of 600°C to 800°C, for example. In region 7 of the shaft furnace, the shaft exhibits an enlarged diameter by comparison to the first axial longitudinal section 8 and second axial longitudinal section 9, so that the reaction gases can be drawn from an annular space 10, as symbolized by the arrow 11. As already described, the reaction gases contain carbon monoxide, carbon dioxide, sodium fluoride, sodium, nitrogen, hydrofluoric acid, hydrogen and possibly beryllium fluoride as primary components. Because the carbon of the used cathode troughs is expended by the gassing reaction, the carbon column or fill 12 present in the shaft furnace, which after all is comprised of the carbon of the used cathode material, drops off in the direction of the arrow 13. Since the reaction gases in region 7 are drawn from the annular space 10, the reaction gases are conducted co-currently with the carbon in the first longitudinal section 8, and counter-currently to the carbon in the second longitudinal section 9 of the shaft furnace. The counter-current process is preferably kinetically imbalanced relative to the Boudouard reaction, thereby maximizing the percentage of carbon dioxide in the waste gas, so that only a short counter-current fill is required. Aside from the ring line 5 for supplying oxygen and/or water/steam in the upper region of the shaft furnace, additional nozzles 14 are secured to the second longitudinal section 9 of the shaft furnace, through which oxygen and/or water/steam can also be blown in. Additional nozzles having the same functionality are located in position 15. Another rotary valve is marked 16, and can be used to discharge calcinate.

While the upper portion of the second longitudinal section 9 exhibiting the nozzles 14 represents a counter-current heating section, the lower region 17 must be understood as a cooling section, since the nozzles 15 are intended for introducing primarily water in liquid form, and possibly as steam or wet steam.

Fig. 2 shows an alternative to the process depicted on Fig. 1. While the carbon is to be completely gassed on Fig. 1, any carbon that has not been gassed can be dissolved in an iron bath 18 in the process according to Fig. 2. Otherwise, the shaft furnace has essentially the same structural design, and in particular also exhibits a region 7 with an enlarged diameter, from which the waste gases can be drawn at position 11. If the iron bath 18 has been saturated with carbon, oxygen is blown into the iron bath via the lance 19, so that pure carbon monoxide escapes at position 20, and can subsequently be thermally utilized. Fluoride-free slag can be tapped at position 21, and relayed for use in the cement industry.

In the alternative configuration of the shaft furnace according to Fig. 3, the iron bath 18 is arranged in the shaft furnace 1, wherein slag is tapped from the fluoride-free slag at position 22. Region 23 of the shaft furnace has a melting zone, in which iron is recarburized. As in the preceding examples, the reaction gas is drawn out of an annular space 10 from the region 7 with an enlarged diameter at position 11.

As may be gleaned from Fig. 4, the system for reprocessing the used cathode troughs is comprised of a quench 24, caustic soda absorber 25 and aerosol demister 26 to go along with the shaft furnace 1. The shaft furnace 1 exhibits the already described features, wherein discharge in this case does not take place via a rotary valve, but rather via a rotating cone 27, which is hollow and can be charged with steam, for example, by way of the line 28, so that the cone releases steam into the interior of the carbon fill like a lance. The reaction gases are again drawn at position 11, wherein the gases are fed into a gas cooler 29 in a first step before getting into the quench 24. They are there reacted with water in aerosol form and depressurized. Sodium fluoride can then be drawn at position 30. The hydrofluoric acid is neutralized by caustic soda in the caustic soda absorber 25. Beryllium fluoride can be drawn from the caustic soda absorber 25 at position 31. In the aerosol demister 26, residual sodium fluoride and beryllium fluoride are separated out of the gas stream, which subsequently represents a pure synthesis gas consisting of carbon monoxide and hydrogen.

As evident from Fig. 5, a lance 33 comprised of an internal pipe 34 and external pipe 35 empties into the lower end 32 of the shaft 4 of the shaft furnace 1. The two pipes 34 and 35 can be displaced or telescoped relative to the shaft furnace and each other, wherein oxygen is introduced into the shaft 4 of the shaft furnace 1 through the internal pipe, and water/steam through the external pipe, for example. Because the lance 33 can be displaced relative to the shaft, the fill 12 in the shaft 4 of the shaft furnace 1 can be mechanically manipulated, thereby breaking mechanical bridges and ensuring discharge in region 36. Secured in region 36 is a pivoting flap 37, upon which the calcinate comes to lie at a natural dumping angle α. Once this dumping angle has been reached, no further discharge of calcinate from the shaft 4 takes place, which in this case causes the flap 37 to pivot into the position 38 denoted with dashed lines, so that the calcinate falls into a discharge sluice 39. The flap 37 is thereupon lifted once more to again gather calcinate.

As further depicted based on the example of Fig. 5, the shaft furnace 1 can generally also exhibit a rectangular cross section instead of a circular cross section. This is represented on Fig. 5 by the wall 43 denoted by dashed lines, wherein at least sections of both the first longitudinal section and second longitudinal section can exhibit a rectangular cross section. A clear width of 600 to 800 mm has here proven beneficial. In order to realize the enlarged cross section required for the central gas vent, the second longitudinal section of the shaft furnace exhibits the wall 44 shown on the right of Fig. 5, which expands toward the discharge opening.

Fig. 6 depicts an alternative embodiment, in which the calcinate is conveyed by means of a vibrating floor 40 in the direction of a screw conveyor 41, so as to in this way also be routed to a discharge sluice 42. The vibrating floor 40 here exhibits an opening for a lance 33.

Fig. 7 presents the upper partial piece of a shaft furnace 1 according to an alternative embodiment, in which the starting material, i.e., the carbon of the used cathode material, is heated to the reaction temperature not via an induction heater encompassing an induction loop, but rather through fossil firing, contrary to the embodiments shown on Fig. 1 to 6. To this end, the first, upper longitudinal section 8 of the shaft furnace 1 incorporates a combustion chamber 45, by way of which fuel, such as natural gas, is supplied to the shaft furnace 1 during its operation. In addition, a ring line 5 leading around the shaft furnace 1 is arranged in the lower region of the first, upper longitudinal section 8 of the shaft furnace 1 at the height of the lower end of the combustion chamber 45, through which oxygen for burning the fuel and gassing the carbon is supplied to the shaft furnace 1. Also provided above the annular shaft 46 separated out of the first, upper longitudinal section 8 by the combustion chamber 45 is a discharge region 2, by way of which the shaft furnace is supplied with a mixture of crushed, used cathode troughs and additive(s), specifically and preferably calcium oxide. For metering purposes, this region of the shaft furnace 1 accommodates a double-bell sluice 47, whose upper part can be displaced in a vertical direction so as to open or close the sluice 47. With the shaft furnace 1 in operation, the mixture of crushed, used cathode troughs and calcium oxide hence passes via the double-bell sluice 47 from the discharge region 2 into the annular shaft 46, in which this mixture encounters the already heated carbon fill. The lower region of the shaft furnace not depicted on Fig. 7 can be configured as in any of the embodiments shown on Fig. 1 to 6. The shaft furnace 1 in this embodiment is preferably operated in such a way as to draw reaction gas with a temperature of about 1200°C at the gas outlet 11. As an alternative to the procedure described above, a mixture of fuel and oxidation gas can also be added to the shaft furnace 1 via the combustion chamber 45, and water or steam, possibly mixed in with oxygen or air, can be introduced through the ring line 5.

Fig. 8 presents an alternative embodiment to the one depicted on Fig. 7, in which the shaft furnace 1 is also fossil fired. Instead of the combustion chamber 45 provided in the shaft furnace 1 on Fig. 7, the shaft furnace 1 on Fig. 8 incorporates a fuel supply line 48 for introducing the fuel in the upper region of its first, upper longitudinal section, through which the shaft furnace 1 is supplied with fuel, in particular natural gas, or a mixture of fuel and oxidation gas, such as oxygen or air. If only fuel is fed to the shaft furnace 1 via the fuel supply line 48, an oxidation gas is fed to the shaft furnace 1 via the ring line 5. In particular if a mixture of fuel and oxidation gas is fed to the shaft furnace 1 via the fuel supply line 48, water or steam, possibly mixed with oxygen or air, can be fed to the shaft furnace 1 via the ring line 5. The shaft furnace 1 is charged by way of the discharge region 2, which for metering purposes can optionally exhibit a rotary valve configured as shown on Fig. 1. The lower region of the shaft furnace not shown on Fig. 8 can be designed just like any of the embodiments depicted on Fig. 1 to 6.

Fig. 9 presents an alternative embodiment to the ones depicted on Fig. 7 and 8, in which the shaft furnace 1 is also fossil fired. Provided instead of the combustion chamber 45 shown on Fig. 7 or the fuel supply line 48 shown on Fig. 8 in the upper region of the shaft furnace 1 on Fig. 9 for purposes of introducing the fuel are lances 19, 19′ extending in the longitudinal direction of the shaft furnace 1, through which oxygen is supplied to the shaft furnace 1, and lances 49, 49′, through which fuel is supplied to the shaft furnace 1. These lances are uniformly arranged concentrically around the longitudinal axis of the shaft furnace 1. A ring line 5 is again provided, through which the shaft furnace 1 can be supplied with oxygen or air and/or water/steam. The lower region of the shaft furnace not shown on Fig. 9 can be designed like any of the embodiments depicted on Fig. 1 to 6.

Reference List

1	Shaft furnace
2	Discharge region for crushed, used cathode troughs and possible additive(s)
3	Rotary valve
4	Shaft
5	Ring line
6	Induction loop
7	Region with enlarged cross section
8	First (upper) longitudinal section
9	Second (lower) longitudinal section
10	Annular space
11	Gas outlet
12	Carbon column / fill
13	Sinking direction of the carbon column / fill
14	Nozzle(s)
15	Nozzle(s)
16	Rotary valve for discharging calcinate
17	Lower region of the shaft furnace
18	Iron bath
19, 19′	Lance for oxygen introduction
20	Gas outlet for carbon monoxide
21	Slag outlet
22	Slag outlet
23	Region/melting zone
24	Quench
25	Caustic lye absorber
26	Aerosol demister
27	Rotating cone
28	Line for steam
29	Gas cooler
30	Position for separating out sodium fluoride
31	Position for drawing beryllium fluoride
32	Lower shaft end
33	Lance

34	Internal pipe of lance
35	External pipe of lance
36	Discharge region
37	Flap
38	Pivoting position of flap
39	Discharge sluice
40	Vibrating floor
41	Screw conveyor
42	Discharge sluice
43	Wall
44	Wall
45	Combustion chamber
46	Annular shaft
47	Double-bell sluice
48	Fuel supply line
49, 49'	Lance for fuel introduction
α	Natural dumping angle

CLAIMS:

1. A method for processing spent carbon-containing cathode material in which the cathode material is placed in a shaft furnace and undergoes a heat treatment in order to gasify carbon at a temperature above the ignition temperature of the carbon and above the vaporization temperature of toxic substances contained in the spent cathode material, wherein in a first longitudinal section of the shaft furnace, the reaction gases are conveyed as a co-current with the carbon and in a second longitudinal section of the shaft furnace, the reaction gases are conveyed as a counter-current to the carbon and in that the reaction gases are withdrawn from a region of the shaft furnace with an enlarged cross section between said longitudinal sections.

2. The method according to claim 1, wherein the spent carbon-containing cathode material is from spent pot liners from the production of aluminium.

3. The method according to claim 1, wherein the reaction gases undergo a subsequent treatment after withdrawal from the shaft furnace.

4. The method according to claim 1 or claim 3, wherein the length of the first longitudinal section is 40% to 80% of the total length of the shaft furnace.

5. The method according to claim 1 or claim 3, wherein the length of the first longitudinal section is 50% to 70% of the total length of the shaft furnace.

6. The method according to claim 1 or claim 3, wherein the length of the first longitudinal section is 60% to 70% of the total length of the shaft furnace.

7. The method according to any one of claims 1 to 6, wherein the length of the second longitudinal section is 20% to 60% of the total length of the shaft furnace.

8. The method according to any one of claims 1 to 6, wherein the length of the second longitudinal section is 30% to 50% of the total length of the shaft furnace.

9. The method according to any one of claims 1 to 6, wherein the length of the second longitudinal section is 30% to 40% of the total length of the shaft furnace.

10. The method according to any one of claims 1 to 9, wherein energy for the heat treatment is introduced into the carbon to be processed by electric induction.

11. The method according to any one of claims 1 to 9, wherein the shaft furnace is heated through fossil firing.

12. The method according to claim 11, wherein fuel or a mixture of fuel and oxidizing gas is fed into the shaft furnace via a combustion chamber disposed in the upper region of the first longitudinal section, via a supply line opening into the upper region of the first longitudinal section.

13. The method according to claim 11, wherein fuel or a mixture of fuel and oxidizing gas is fed into the shaft furnace via a combustion chamber disposed in the upper region of the

first longitudinal section, via one or more lance(s) disposed in the upper region of the first longitudinal section.

14. The method according to claim 11, wherein fuel or a mixture of fuel and oxidizing gas is fed into the shaft furnace via a combustion chamber disposed in the upper region of the first longitudinal section, via a supply line opening into the upper region of the first longitudinal section and via one or more lance(s) disposed in the upper region of the first longitudinal section.

15. The method according to any one of claims 1 to 14, wherein oxygen is blasted into the first longitudinal section of the shaft furnace.

16. The method according to any one of claims 1 to 14, wherein oxygen is blasted into the second longitudinal section of the shaft furnace.

17. The method according to any one of claims 1 to 14, wherein oxygen is blasted into the first and second longitudinal sections of the shaft furnace.

18. The method according to any one of claims 1 to 17, wherein water or steam is blasted into the first longitudinal section of the shaft furnace.

19. The method according to any one of claims 1 to 17, wherein water or steam is blasted into the second longitudinal section of the shaft furnace.

20. The method according to any one of claims 1 to 17, wherein water or steam is blasted into the first and second longitudinal sections of the shaft furnace.

21. The method according to any one of claims 1 to 20, wherein oxygen and water or steam are blasted into the shaft furnace with the aid of lances.

22. The method according to any one of claims 1 to 21, wherein non-gasified carbon is dissolved in an iron bath.

23. The method according to any one of claims 1 to 22, wherein an additive in order to slag the refractory material is added to the spent carbon-containing cathode material when it is introduced into the shaft furnace or beforehand.

24. The method according to claim 23, wherein the additive is a calcium compound.

25. The method according to claim 23, wherein the additive is a magnesium compound.

26. The method according to claim 23, wherein the additive is a calcium compound and a magnesium compound.

27. The method according to claim 23, wherein the additive is a compound selected from the group consisting of calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate and any mixtures of two or more of said compounds.

28. The method according to claim 23, wherein the additive is calcium oxide.

29. The method according to any one of claims 1 to 21, 23 to 28, wherein the carbon of the cathode material is completely gasified and the residual calcined coke is discharged.

30. The method according to any one of claims 1 to 29, wherein the basicity in the shaft furnace is adjusted by adding basic or acidic aggregates.

31. The method according to claim 30, wherein adding basic or acidic aggregates comprises adding CaO or SiO_2.

32. The method according to claim 30 or claim 31, wherein the basic and acidic aggregates are added alternately.

33. The method according to any one of claims 1 to 32, wherein unused graphite or coke is added in addition to the carbon of the spent cathode material.

34. The method according to any one of claims 1 to 33, wherein the reaction gases are withdrawn at a temperature of 800°C to 1,200°C and conveyed to the subsequent treatment.

35. The method according to any one of claims 1 to 33, wherein the reaction gases are withdrawn at a temperature of 900°C to 1,000°C and conveyed to the subsequent treatment.

36. The method according to any one of claims 1 to 33, wherein the reaction gases are withdrawn at a temperature of 1,000°C and conveyed to the subsequent treatment.

37. The method according to any one of claims 1 to 36, wherein the reaction gas withdrawn from the shaft furnace is supplied to a cooled, fluidized bed reactor which contains

particles of aluminium oxide, and cleaned effluent gas is withdrawn from the fluidized bed reactor.

38. The method of claim 37, wherein the fluidized bed is isothermally operated.

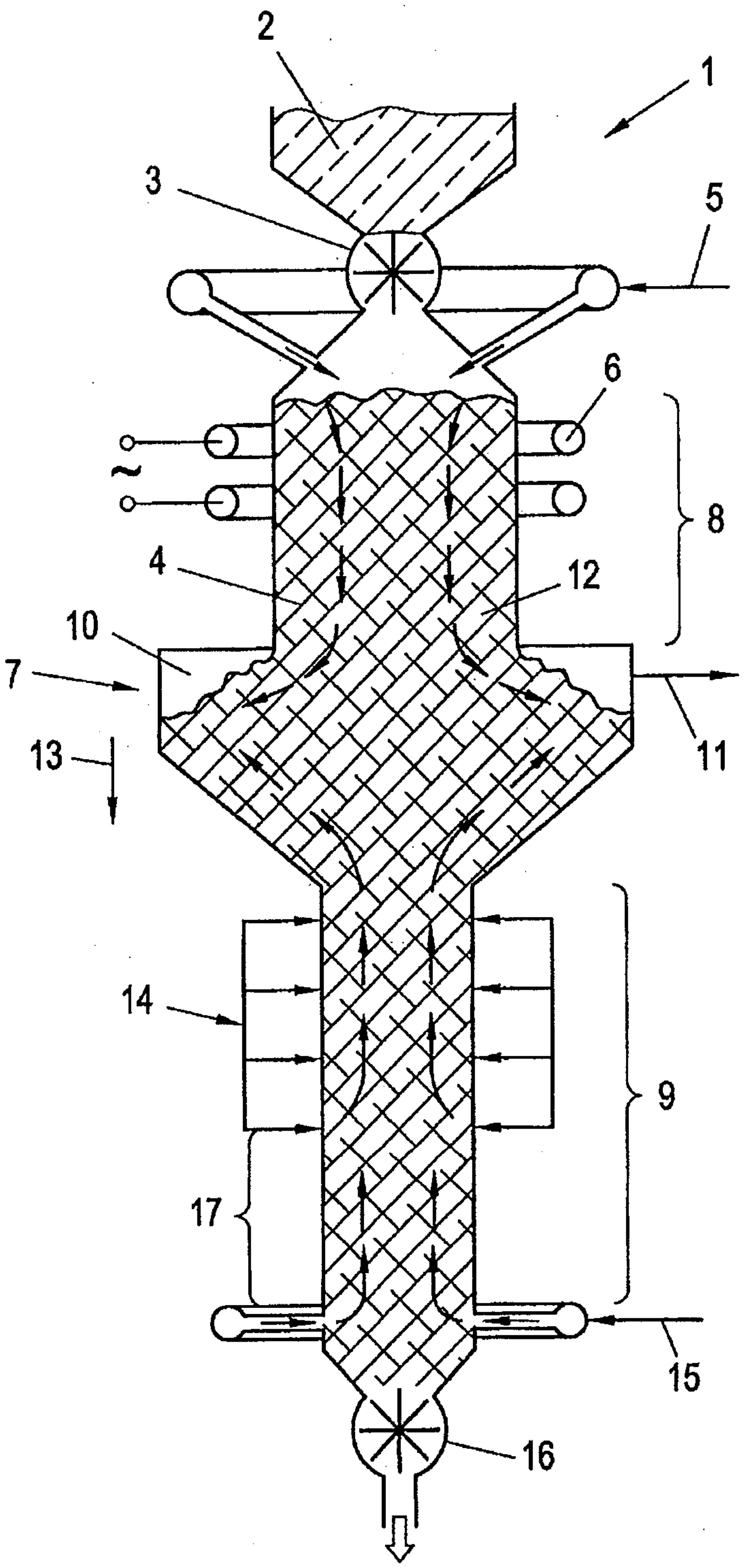


Fig. 1

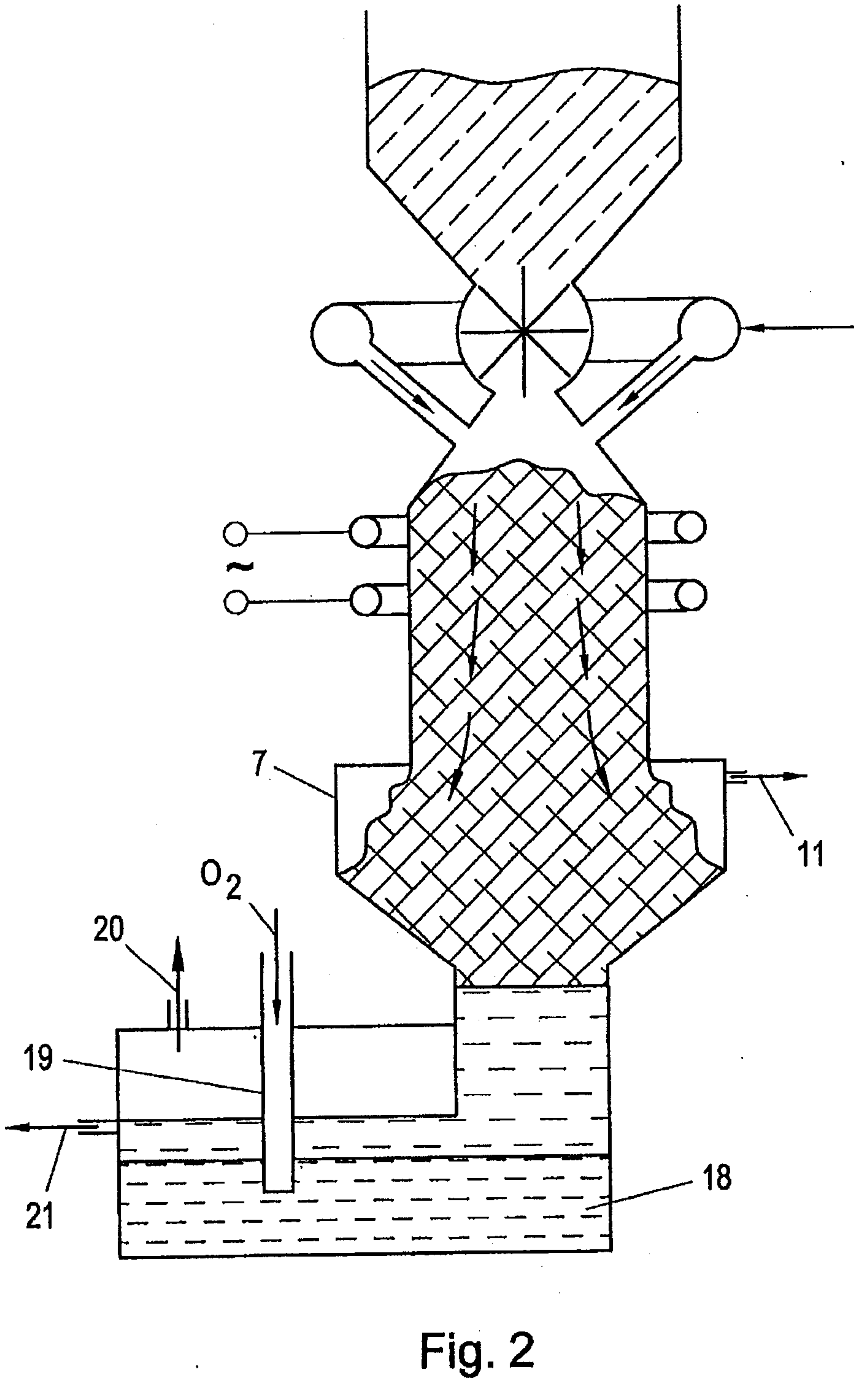


Fig. 2

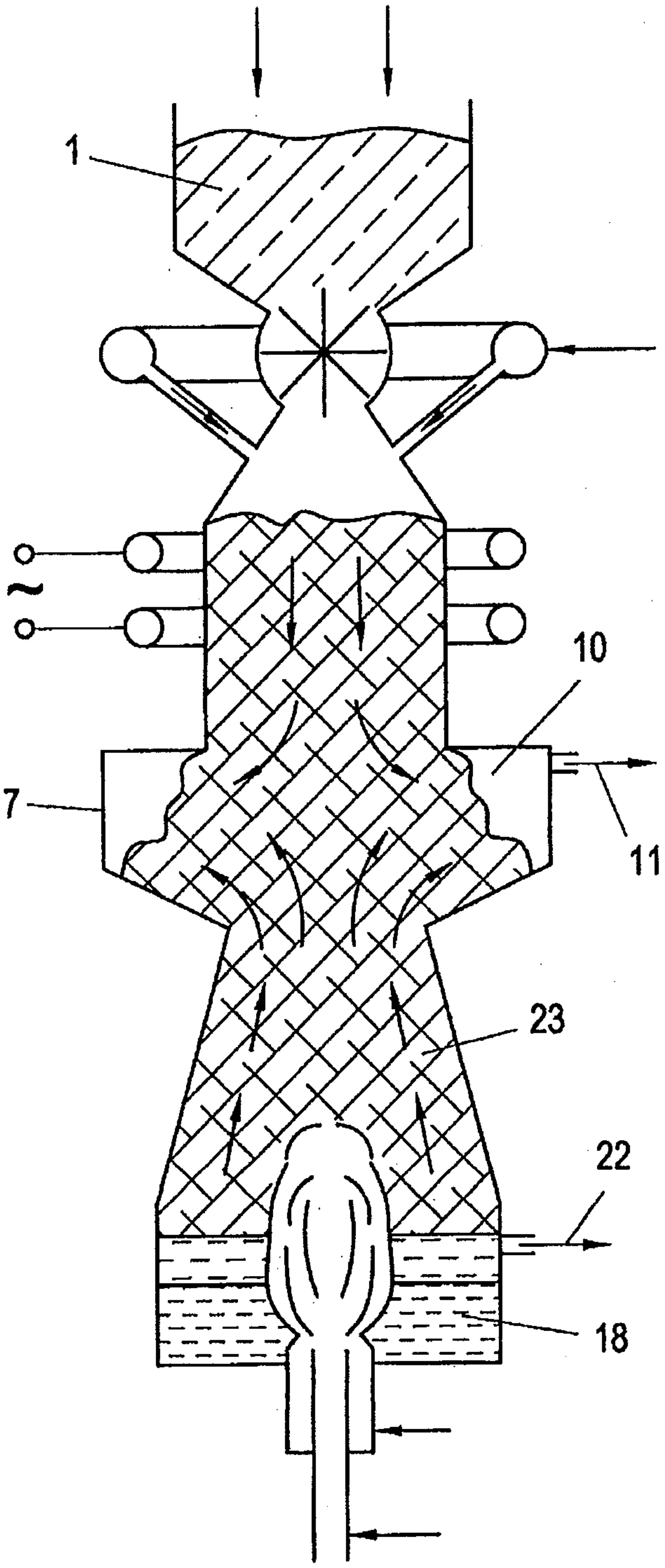


Fig. 3

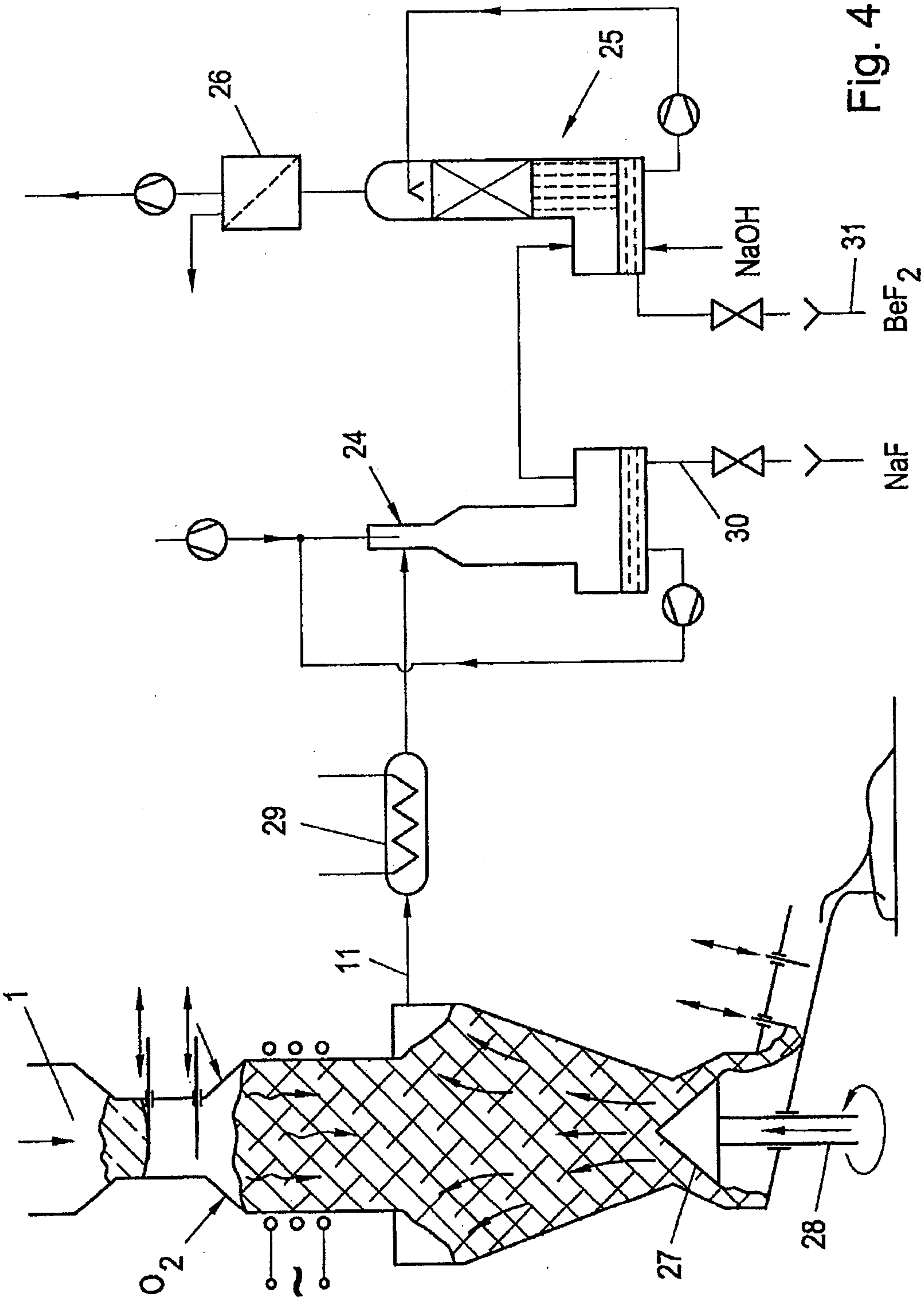


Fig. 4

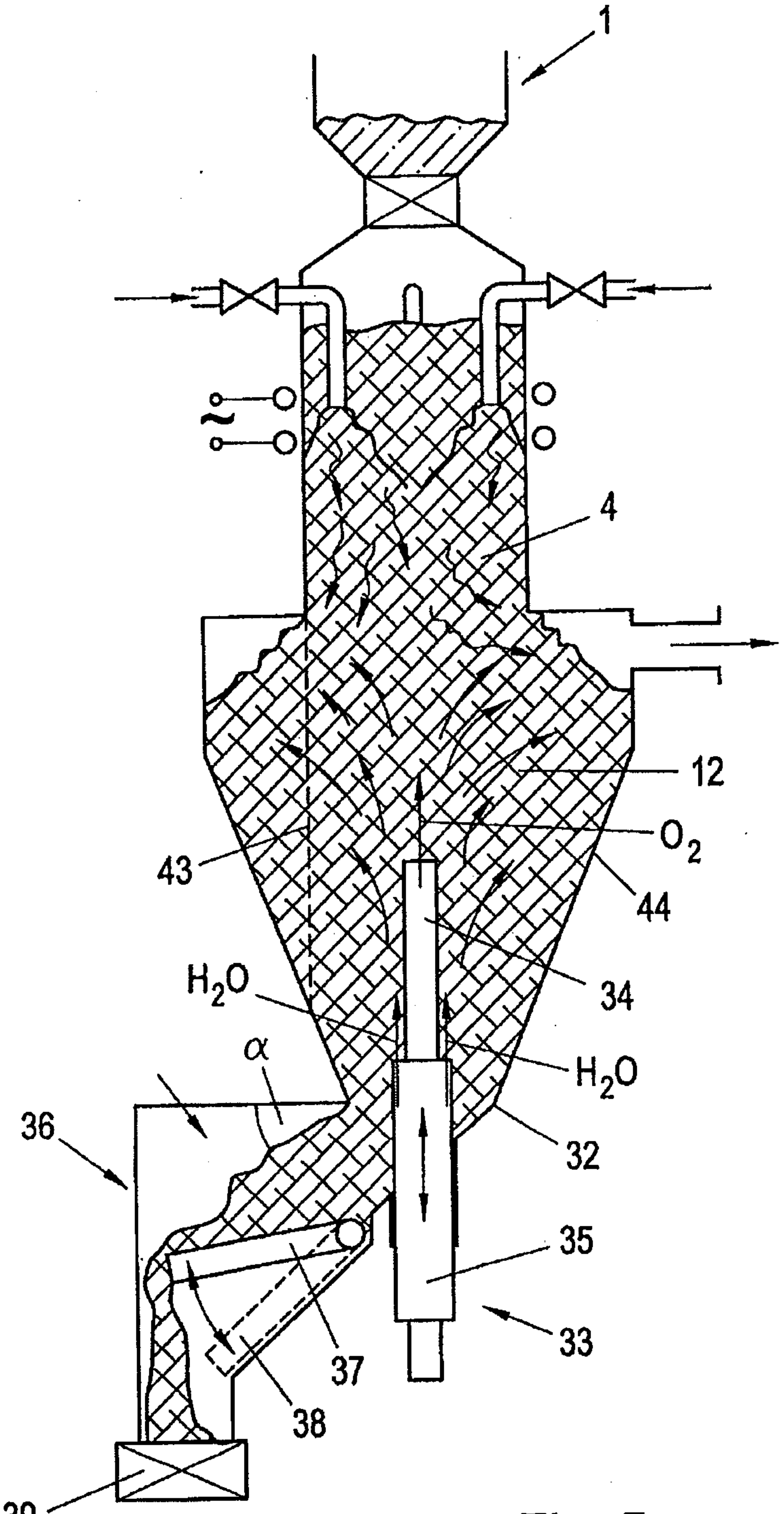


Fig. 5

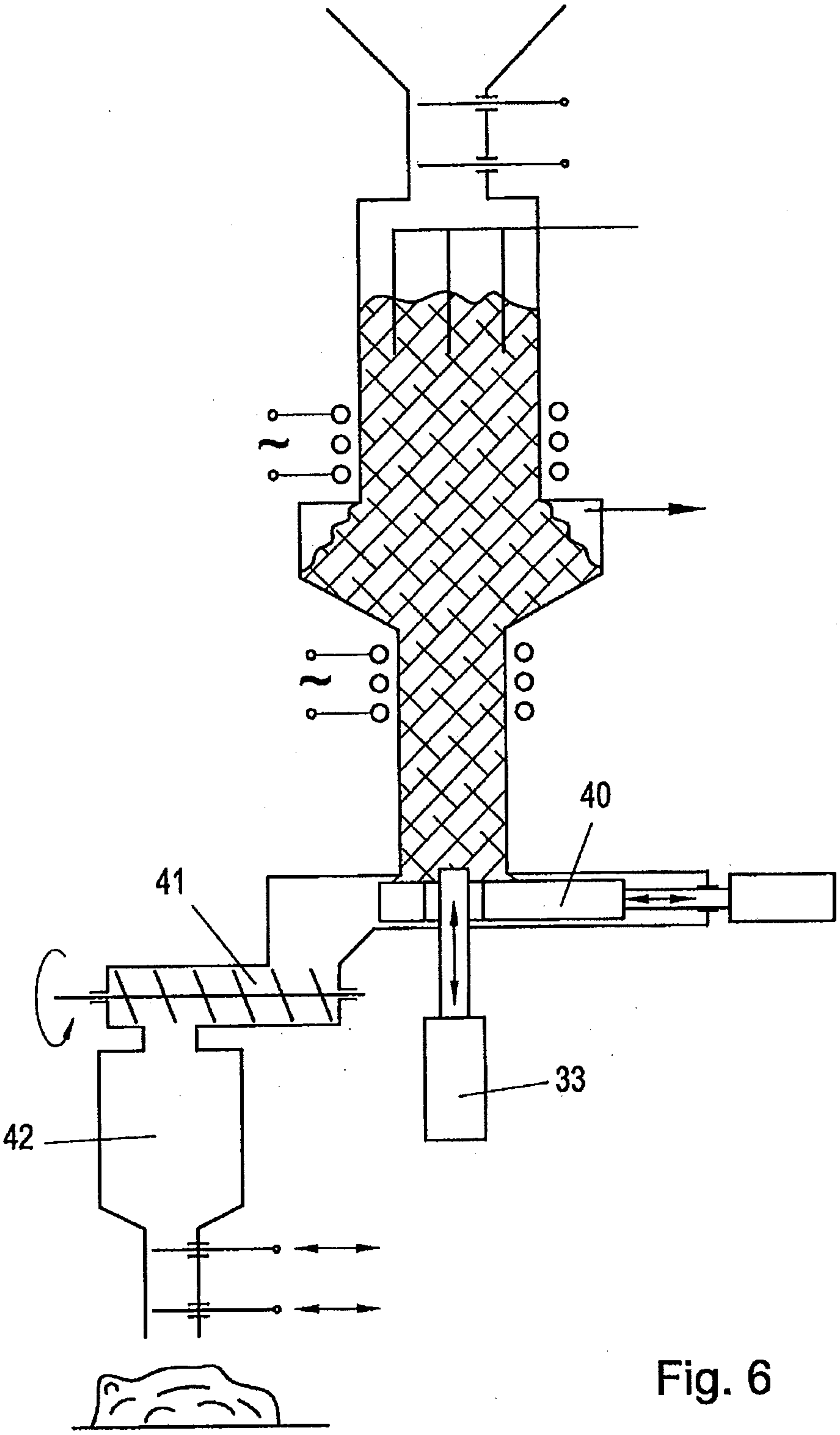


Fig. 6

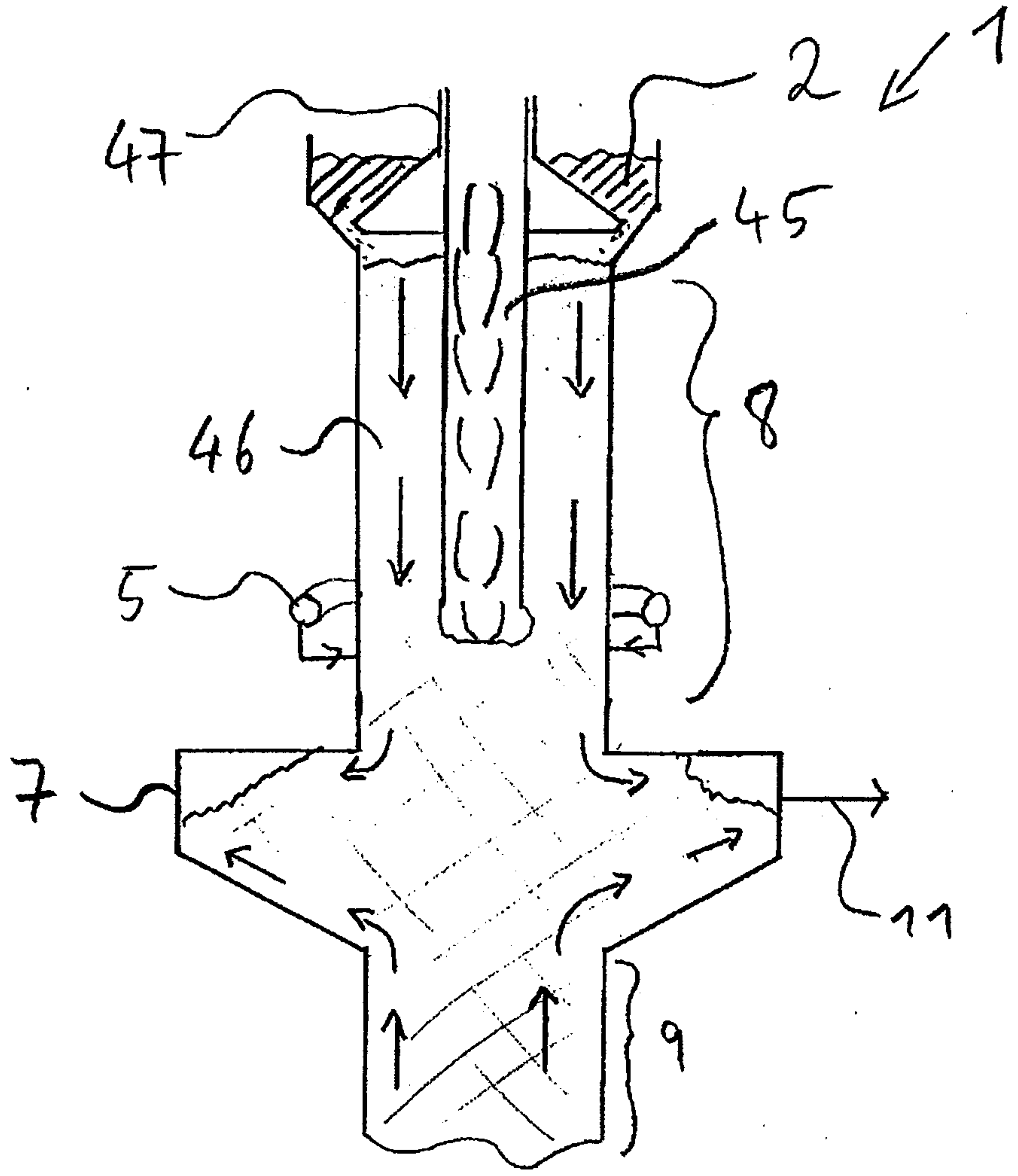


Fig. 7

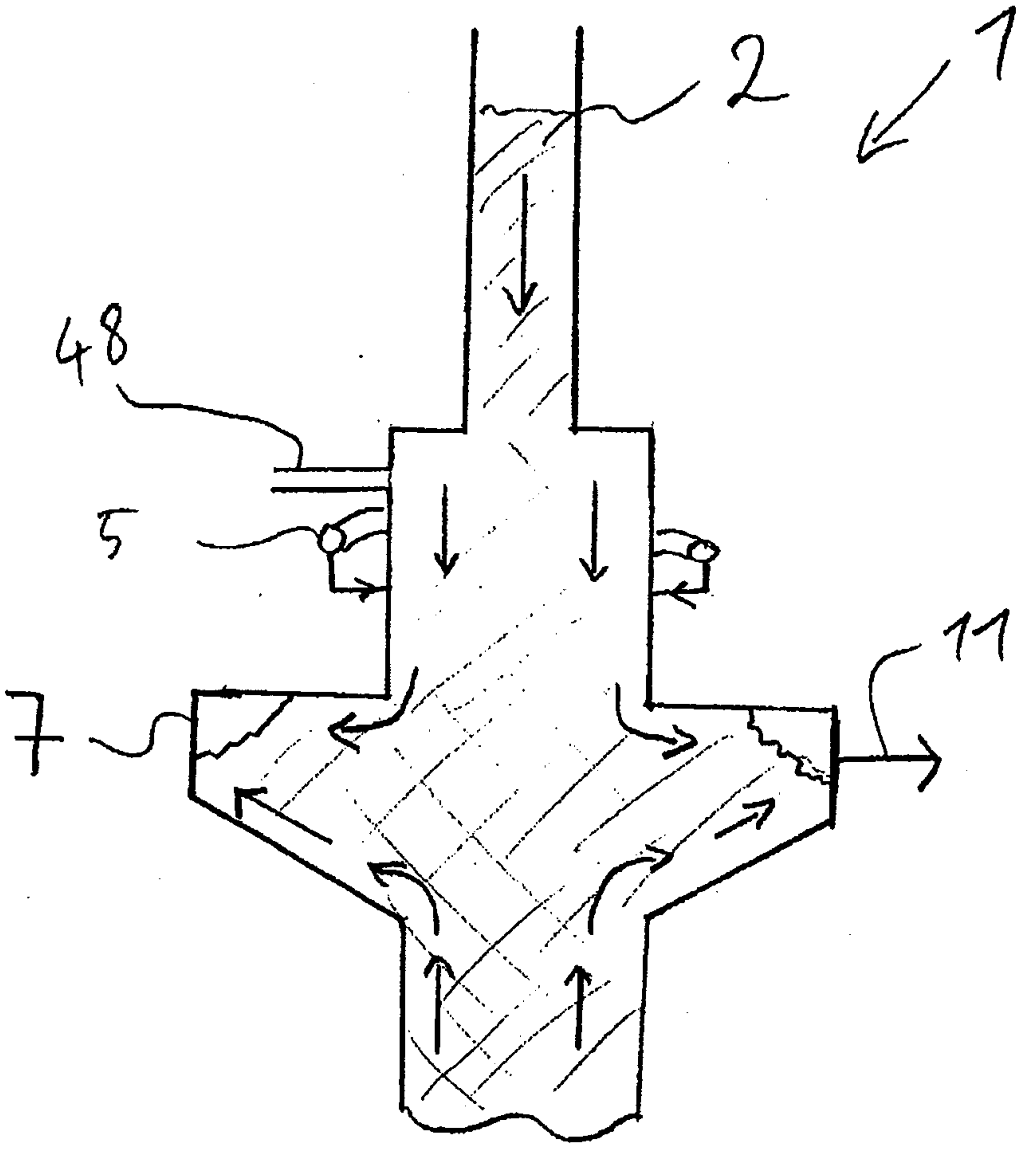


Fig. 8

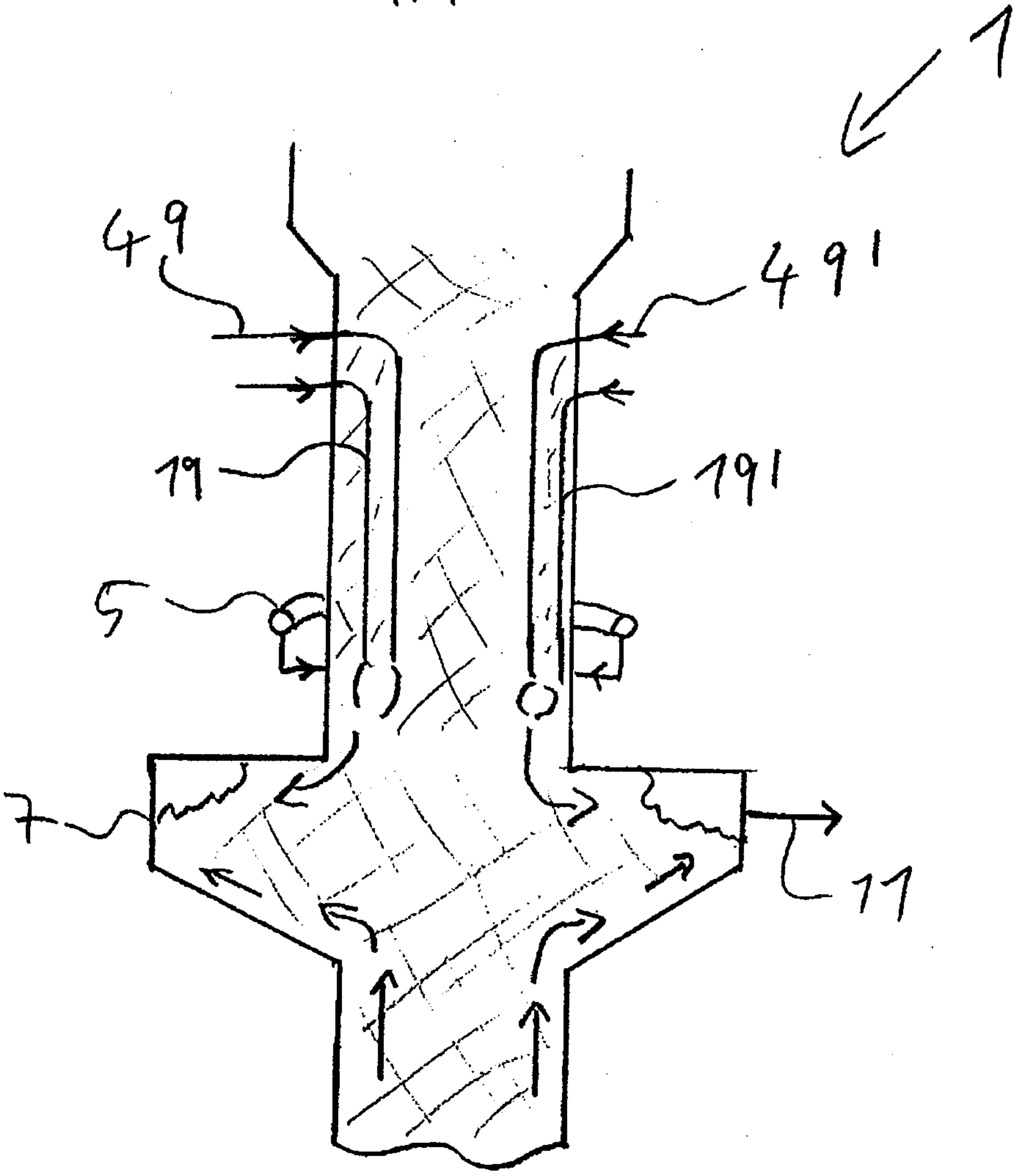
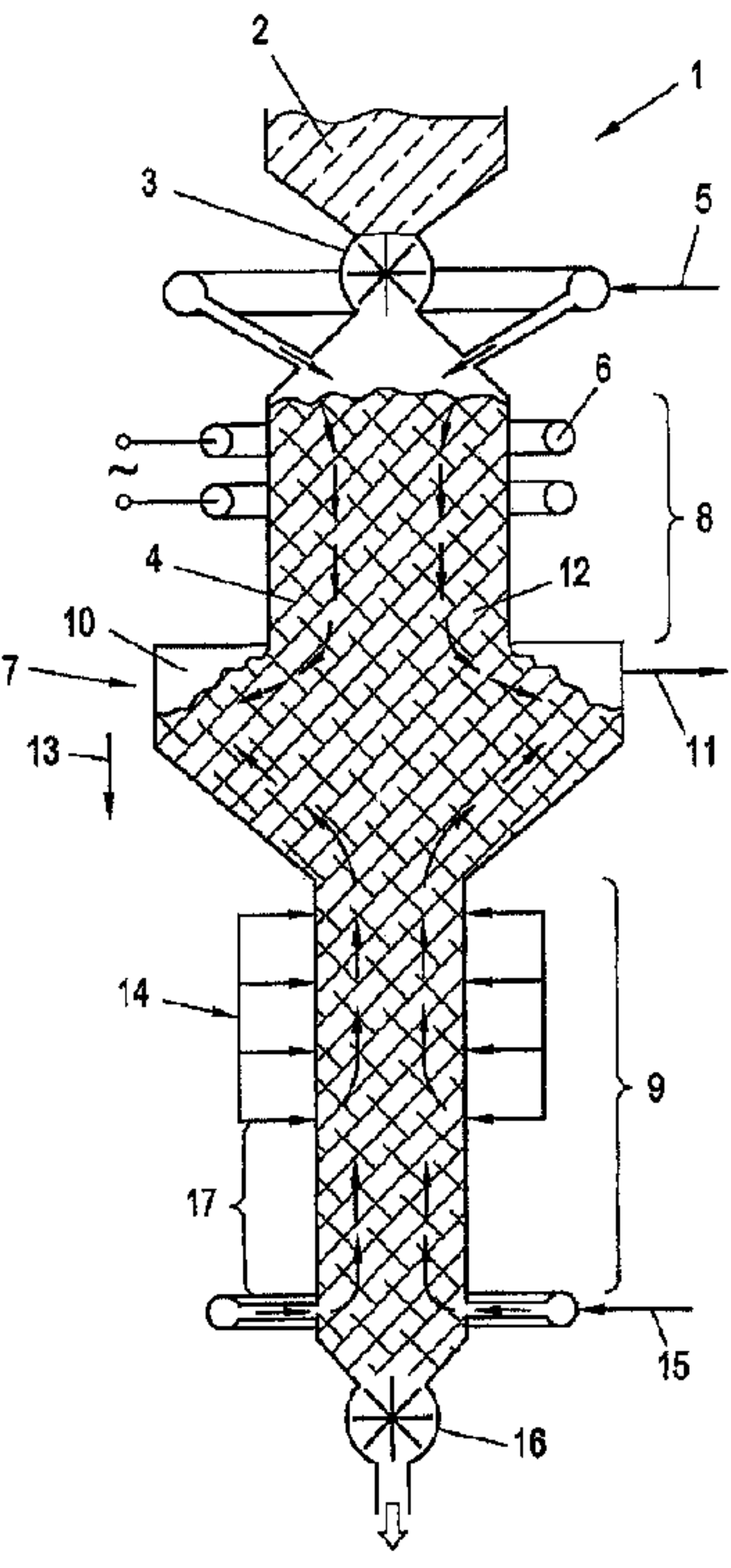


Fig. 9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