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(54) Title: METHOD FOR CALCINING CARBONATE MINERAL STONES IN A PARALLEL FLOW REGENERATIVE KILN AND IMPLEMENTED KILN

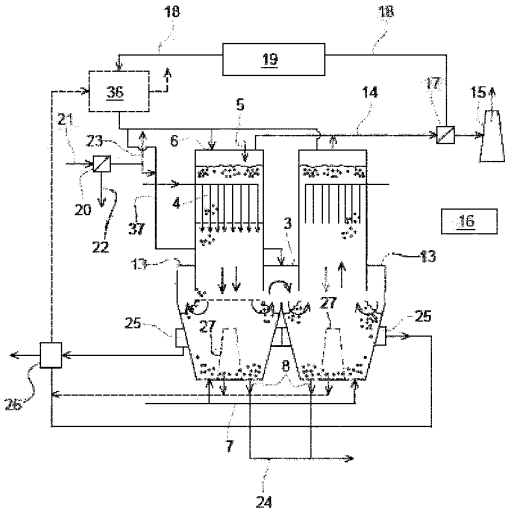


FIG. 2

(57) Abstract: Method for calcining carbonate mineral stones in a parallel flow regenerative kiln wherein through said connecting channel, where a mixing gas stream is injected through a series of mixing gas entry means at high velocity in such a way that a ratio of momentum J between each gas stream and the combustion fumes is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel.

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Method for calcining carbonate mineral stones in a parallel flow regenerative kiln and implemented kiln.

The present invention relates to a method for calcining carbonate mineral stones in a parallel flow regenerative kiln (PFRK). Such a kiln comprises at least two shafts interconnected by means of a connecting channel. In each shaft the stones are introduced in a top portion and follow a downward gravity displacement during which the stones are successively preheated, calcined and thereafter cooled in order to be collected in a low portion of each shaft.

By the terms "stones, carbonate mineral stones, limestone stones", it is meant according to the present invention pieces of raw carbonated material having a mean particle size d_{50} comprised between 20 mm to 20 cm, preferably higher than 25 mm, preferably lower than 18 cm, more preferably lower than 16 cm, and typically between 3 and 15 cm.

By "connecting channel", it is meant according to the present invention, all the ducting and spaces void of stones that allow the combustion gases to flow from the shaft in calcining mode to the shaft(s) in preheating mode. This connecting channel comprises one or several crossover channels and possibly peripheral channels.

By "crossover channel", it is meant according to the present invention, the straight part (as seen from top) of the connecting channel located between two shafts. If peripheral channels are existing, the peripheral channels of two shafts will be connected by a crossover channel.

By "peripheral channel", it is meant according to the present invention, the part of the connecting channel located at the periphery, or around a shaft, particularly in the case of a circular shaft, at the

exception of the part of the periphery already occupied by the crossover channel.

Carbonate mineral according to the present patent application is typically a calcium-magnesium carbonate, also known as limestone, when containing low amount of magnesium, and dolostone, when the magnesium content is close to the one of calcium on a molar basis.

A Parallel Flow Regenerative Kiln usually has 2 to 3 shafts, of circular or rectangular section, which do not work in a continuous way. In standard operation, in every period, usually of 12 to 20 minutes, fuel is injected inside a calcining zone of one shaft by means of lances and is burned in presence of combustion air. Thereafter the descending calcined product is cooled in a cooling zone by heat exchange with a cooling air introduced at the bottom of the shaft. The flue gas comprises or consists of the combustion fumes, the gas of decarbonation and the heated cooling air. This flue gas is drawn into another shaft (or the 2 other shafts) through the connecting channel and goes thereafter through the stones present in this shaft (or those 2 other shafts) and thereafter outward the kiln. So, in this "preheating" shaft(s), the stones are preheated by the exiting flue gas. Consequently, during this period the shaft wherein the combustion takes place works according to a calcining mode and the shaft(s) wherein the flue gas is drawn through the stones works according to a preheating mode. Thereafter, there is a period, usually between 30 seconds and 2 minutes, called inversion period, which is provided, notably for reverting the air and fuel circuits. And the shaft having worked in a calcining mode works now in a preheating mode and the shaft (or one of the 2 other shafts) having worked in a preheating mode works now in a calcining mode.

The classical method for calcining carbonate mineral stones in a parallel flow regenerative kiln having at least two shafts

interconnected by a connecting channel, comprises, in standard operation,

- loading carbonate mineral stones at the top of each shaft,
- preheating these loaded stones in a preheating zone,
- calcining these preheated stones in a calcination zone with production of a decarbonated calcined material,
- cooling the calcined material with cooling air in a cooling zone, with formation of a heated cooling air, by heat exchange,
- discharging the calcined material from the bottom of the shafts,
- exhausting a gaseous effluent from the kiln,
- each shaft alternately working in a calcining mode and in a preheating mode, one shaft working in a calcination mode during a predetermined time period during which at least another shaft works in a preheating mode, and inversely,
- the calcining mode comprising :

said loading step of carbonate mineral stones at the top of a kiln shaft,

said calcining step by means of an increase of temperature inside said carbonate mineral stones having been preheated, with production of said decarbonated calcined material and release of a gas stream which flows in co-current with the calcined material, and

through said connecting channel, a passage of said gas stream toward the at least one shaft working in a preheating mode,

- said preheating mode comprising :

said preheating step of the loaded carbonate mineral stones by heat exchange with said gas stream coming from the connecting channel, which is ascending and flows in counter-current through the loaded carbonate mineral stones, and

said exhausting step of said gas stream as gaseous effluent at the top of said at least one shaft in preheating mode,

said cooling step comprising a supply of cooling air at the bottom of each of said shafts or only of the shaft working in the calcining mode.

In the calcining zone of a classical kiln, it is required in calcining mode to inject and burn a fuel into the mass of the stones to be calcined under the preheated stones in order to benefit from the heat of the flue gas that was transferred to the stone in the preheating zone. In preheating mode, the stones introduced into the kiln are at ambient temperature and the flue gas drawn outside the kiln has a temperature typically comprised between 80 and 250°C, preferably between 100 and 200°C and generally at about 150°C, limiting the energy losses.

According to the invention, standard operation means that the kiln produces the calcined material in a continuous manner. This operation does not concern the phases of starting, stopping or maintenance of the kiln.

According to the invention, carbonate mineral stones particularly mean calcareous stones (limestones), dolomitic stones (dolostones or unburnt dolomites) and/or magnesite stones which are calcined into quicklime, (quick) dolime and/or magnesia, respectively.

The calcination reaction of limestone into quicklime is :

$CaCO_3$ (solid) + heat ➔ CaO (solid)+ CO_2 (gas)

This is a reversible endothermic reaction and the lime recombines with the CO_2 at the first opportunity below 900°C, with an equilibrium and more or less fast kinetics depending on the temperature and the ambient concentration of CO_2. Below 850 to 900°C lime and CO_2 can easily recombine. But from a temperature of the order of 900°C the starting stones give off a significative volume of CO_2 during their decarbonation. In order to obtain such a decarbonation, the temperature must consequently be significatively increased in the calcining zone. Today this increase is mainly obtained by combustion of a fuel, frequently fossil, in presence of an oxidizer such as air. In turn this fuel

combustion contributes also to an important release of CO_2. Globally the current calcination methods actively participate in increasing the greenhouse effect.

This common calcination method also has the disadvantage that the fuel is burnt with air and the calcined product is cooled by air. This results in a gaseous effluent being released at the top of the furnace having a high level of diatomic nitrogen and a comparatively low level of CO_2 (volume concentration of about 20% to 27% on dry gas) which is costly to capture because of the large presence of dinitrogen from the air used.

To capture this CO_2, it may be considered to use an "end-of-pipe" method of CO_2 concentration and abatement, notably cryogenic or by chemical solvent called "amines", which is the most widespread technique applied to the furnace fumes at the end of the line, after the dust collection filter However, for carrying out end-of-pipe methods as aforementioned, constrains are existing, notably in terms of concentration of CO_2, but also in terms of compliancy of the fumes, which may require intermediate devices, the price and the use of hazardous solvents .

More recently, to be able to capture the CO_2 emitted in a PFRK furnace, operating PFKR in oxy-combustion has been proposed (see for example JP2002060254. However, the concentration of CO_2 in the exhaust effluent is still below 50 % vol on a dry basis.

For the same purpose, it has also been proposed to replace all the air from the method, combustion air carrying the solid fuel and cooling air, with recycled combustion fumes and introducing pure oxygen into the shaft in calcining mode (see CN105000811). For any person skilled in the art, it is clear that this process is unfeasible, since the lime will recarbonate during cooling. As seen above, the CO_2 cannot be recirculated to cool the lime, since the lime will immediately recombine with this CO_2 to form again a carbonate, notably $CaCO_3$. On the other hand, using pure oxygen at the top of the furnace poses serious problems in terms of material compatibility (notably due to excessive temperature)

and this input will not be a sufficient mass flow to effectively recover the heat accumulated in the regeneration area. The disadvantages and feasibility problems of this method have also been discussed in the patent application US2020/0048146.

It should also be noted that the cooling air in the PFRK, in contrast to the rotary kiln, for example, does not play a significant role on the combustion and the calcination process in the shaft in calcining mode.

Standard mode means that the furnace is in normal service during which it continuously produces calcined material. This mode therefore does not apply to the start-up and shut-down phases of the furnace or to maintenance in the event of a malfunction.

Variation of the common calcination process have been proposed in order to improve capture of CO_2, such as for example in WO2022/002869 or WO2022/229120.

In PFRK kilns operation with a regular combustion of fuel in presence of combustion air, the mixing between fuel and comburant gas is relatively poor in the combustion shaft. This leads to CO generation. The generated CO is typically reburned in contact with the cooling air that comes in contact with the combustion fumes in the connecting channel or a bit earlier. Even if the mixing of these two streams is relatively poor, the vast excess of cooling air allows to reburn the CO at the level of the connecting channel.

In PFRK kiln working in oxy-combustion, the exhaust gaseous effluent should be as concentrated in CO_2 as possible. Accordingly, there has been some proposal to produce concentrated exhaust gas. One proposal that was discussed above is to replace the cooling air by exhaust gaseous effluent such as disclosed in CN10500081 and in JP2002060254. Other proposals are to isolate the cooling air from the exhaust gaseous effluent (see W02022/238385, WO2022/238384 or WO2022/229120).

In WO2022/002869, it was proposed to extract the cooling air in a ring collector, through a collector tunnel or through a central device,

located below the connecting channel to avoid as much as possible mixing between the exhaust gaseous effluent concentrated in CO_2 and the cooling air.

In the absence or limited residual presence of cooling air, the aforementioned CO reburning by the cooling air will not occur.

In addition, according to WO2022/002869, to reach high CO_2 concentration and ensure complete combustion, the kiln is likely to be operated under excess of oxygen with respect to the combustion stoichiometric conditions. However, it is expected that the excess of oxygen during combustion is going to be as limited as possible to avoid dilution of the CO_2 in the exhaust effluent. This obviously increases the risk of high CO generation.

CO would have to be treated before CO_2 capture and end-of-pipe solutions, such as Regenerative Thermal Oxidation, are CAPEX and OPEX expensive.

There is therefore a need to provide a method to be carried out in PFRK without changing the cyclical operation thereof and with few or no changes to the structure thereof while making it possible to capture the CO_2 present in the gaseous effluents emitted by the furnace and therefore where the CO concentration in the exhaust effluent is as limited as possible to avoid expensive CO treatment,

To solve these problems, the present invention provides a method for calcining carbonate mineral stones in a parallel flow regenerative kiln having at least two shafts interconnected by a connecting channel, comprising, in standard operation,

- loading carbonate mineral stones at the top of each shaft,
- preheating these loaded stones in a preheating zone,
- calcining these preheated stones in a calcination zone with production of a decarbonated calcined material,
- cooling the calcined material with cooling gas in a cooling zone, with formation of heated cooling gas by heat exchange,

- discharging the calcined material from the bottom of the shafts,

- exhausting a gaseous effluent from the kiln,

- each shaft alternately working in a calcining mode and in a preheating mode, one shaft working in a calcination mode during a predetermined time period during which at least another shaft works in a preheating mode, and inversely after activation of the inversion means,

- the calcining mode comprising :

- in the presence of said preheated carbonate mineral stones descending into said shaft, oxy-combusting fuel in the presence of oxygen so as to obtain said calcination of said stones in said combustion zone, and the decarbonation thereof into calcined material with the release of combustion fumes descending co-currently in the shaft in calcination mode, and
- through said connecting channel, a passage of said combustion fumes toward the at least one shaft working in a preheating mode, where a mixing gas stream is injected through a series of mixing gas entry means at high velocity in such a way that a ratio of momentum J between the each gas stream and the combustion fumes is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel

- said preheating mode comprising :

- said preheating step of the loaded carbonate mineral stones by heat exchange with said combustion fumes depleted in CO coming from the connecting channel, which is ascending and flows in counter-current through the loaded carbonate mineral stones, and
- said exhausting step of said combustion fumes depleted in CO as gaseous effluent at the top of said at least one shaft in preheating mode,

said method further comprises

- recirculating a fraction of the gaseous effluent exhausted from the top of said at least one shaft in preheating mode,
- injecting the gaseous effluent, exhausted from the top of said at least one shaft in preheating mode, to the shaft in calcining mode, either under the form of a comburant mixture or with an injection of a combustion stream containing a comburant, for said step of oxy-combusting the fuel.

As it can be seen, the method according to the present invention carries out fuel combustion in dioxygen which results in the mixing gas stream containing the combustion fumes and in the calcination of the carbonate stones. This produces mainly CO_2 and steam with some impurities, present as traces in the fuel and in the material to be calcined, and some oxygen not used up by the fuel combustion.

Naturally, these combustion fumes also contain the CO_2 supplied to the oxidizing mixture. This evidently results in a significant increase in the CO_2 content of the gaseous effluent discharged from the top of the furnace, compared to the conventional method.

According to the invention, a gaseous effluent concentrated in CO_2 means that it has a CO_2 content of at least 60%, more preferably of at least 70%, more particularly of at least 75%, especially at least 80% and particularly advantageously at least 90% by volume on dry gas. This CO_2 can then be used or sequestered under favorable conditions, drastically decreasing the contribution of the furnace to the greenhouse effect.

The use of this oxy-combustion method does not necessarily require any particular design of the furnace itself. The only changes to be made to the furnace may be simply external to the furnace and consist of changing the effluent circuits leaving the furnace and providing at least one source of concentrated dioxygen.

To reduce the CO concentration in the exhaust effluent, through said connecting channel, during the passage of said combustion fumes towards the at least one shaft working in a preheating mode a mixing gas stream is injected through a series of mixing gas entry means, such as a series of nozzle(s) or orifices connected to respective pipes, at high velocity in such a way that a ratio of momentum J between the gas stream and the combustion fumes is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel.

Within the meaning of the present invention, the momentum of a fluid flow is defined as the mass flow of this fluid (in kg/s) multiplied by its average velocity (in m/s). It is expressed in Newtons ($kg*m/s^2$). The momentum ratio between a mixing gas stream and the combustion fumes flow is defined as the ratio of the momentum of the mixing gas stream and the momentum of the combustion fumes. The momentum of the mixing gas stream is measured at the mixing gas outlet. The momentum of the combustion fumes is measured at the cross-section perpendicular to its flow direction and intersecting the center of the mixing gas entry means.

In order to complete the combustion of the CO, an intense mixing of the combustion fumes with comburant gas must be ensured. This is obtained by jet mixing, i.e. the injection of a mixing gas stream through entry means at high velocity in the connecting channel.

Advantageously, said ratio of momentum J is higher or equal to 2, more preferably higher or equal to 4, more preferably higher or equal to 5, more preferably higher or equal to 6, in particular higher than or equal to 7, more particularly higher than or equal to 8, even higher than or equal to 9 or higher than or equal to 10 or higher than or equal to 11 or higher than or equal to 12 or higher than or equal to 13 or higher than or equal to 14 or higher than or equal to 15 or higher than or equal to 16 or higher than or equal to 17 or higher than or equal to 18 or higher than or equal to 19 or higher than or equal to 20 or higher than or equal to 21 or higher than or equal to 22 or higher than or equal to 23 or higher than or equal to 24 or higher than or equal to 25 or higher than or equal to 26 or

higher than or equal to 27 or higher than or equal to 28 or higher than or equal to 29 or higher than or equal to 30 to ensure a good mixing between the mixing gas stream and the exhaust effluent.

It must be noted that the mixing gas stream does not require to be continuous or constant. It can be advantageous to enhance mixing to supply the mixing gas stream in the form of jets incorporating periodic oscillations. Such periodic oscillations can notably take the form of intermittent pulsed jets, but also include sinusoidal oscillations in flow, pressure or velocity, or other shapes of oscillation waves. In the case of jets with periodic oscillations, including pulsed jets, the momentum shall be calculated using the average properties of the jet over the duration of several oscillations or pulsations.

Preferably, the loading of carbonate mineral stones occurs during the inversion period at the top of the shaft that will work in a preheating mode after said inversion period. Alternatively, or in addition, the loading of carbonate mineral stones occurs at the top of the shaft that works in a preheating mode or at the top of the shaft that works in a calcination mode. Preferably, the loading of carbonate mineral stones occurs at the top of the shaft that works in a preheating mode.

According to the present invention, advantageously, said mixing gas stream is chosen in the group consisting of a CO_2-rich mixing gas stream, a O_2-rich mixing gas stream, a steam mixing gas stream or a mixture thereof, to be compatible with oxyfuel or oxy-combustion CO_2 concentration.

More particularly according to the present invention, said mixing gas stream is pressurized before passing through the series of mixing gas entry means to reach a differential pressure between said mixing gas stream and the gas inside the connecting channel comprised between 100 mbar and 10 000 mbar, preferably between 200 and 1000 mbar to achieve high velocity.

In a preferred embodiment of the method according to the present invention, said mixing gas stream is heated before passing the

series of mixing gas entry means to a temperature comprised between 10 °C and 1000 °C, more preferably between 50°C and 1000°C, most preferably between 75°C and 800°C, as the increase of temperature will increase volume and therefore the (injection) velocity.

According to a particular embodiment, the exhaust effluent is partially or fully collected in at least one buffer after said exhausting step to absorb fluctuation due to the operation of the kiln, especially during the inversion phase. The presence of the buffer ensures a regular feeding of exhaust effluent to the kiln or to any downstream device, such as purification and/or concentration units, filters, …

By the terms "at least one buffer", it is meant according to the present invention at least one device of any kind of gas storage allowing to store at least the quantity corresponding to 10 seconds of the gas flow in the connected pipe.

According to another particular embodiment of the present invention, said combustion stream containing a comburant is chosen amongst O_2-rich gas mixture, in particular pure oxygen, a steam-based gas mixture containing oxygen or their mixture..

Preferably, by the terms O_2-rich gas mixture, it is meant according to the present invention, a mixing gas stream containing more than 70 vol% on dry basis of di-oxygen with respect to the volume of combustion stream containing a comburant, more preferably a mixing gas stream containing more than 80 vol%, even more than 90 vol%, more particularly more than 93 vol% on dry basis di-oxygen, with respect to the volume of combustion stream containing a comburant, such as for example oxygen generated by pressure swing adsorption method which has generally a O_2 concentration of 93 vol% on dry basis di-oxygen.

Preferably, when the combustion stream is a mixture of steam and O_2-rich gas mixture, the volume ratio between steam and the O_2-rich gas mixture is of at least 10-90, at least 20-80, at least 30-70, at least 40-60, at least 50-50, at least 60-40, at least 70-30, at least 80-20, at least 90-10.

According to the present invention, in a preferred embodiment, oxygen is introduced in the kiln at one or more locations to provide a total amount of oxygen introduced in the kiln higher than the amount required for a stoichiometric combustion for the oxy-combustion of fuel in presence of oxygen in excess, and is preferably is introduced at an excess from 2 to 30%, preferably from 3 to 20 %, in particular from 4 to 17%, advantageously from 5 to 15 % in volume with respect to the stoichiometric need of the combustion reaction.

In other words, the total amount of oxygen introduced in the kiln is equal to the amount of oxygen needed for a stoichiometric combustion for the oxy-combustion of fuel in presence of oxygen multiplied by an excess factor from 1.02 to 1.30, preferably 1.03 to 1.2, in particular from 1.04 to 1.17, advantageously from 1.05 to 1.15.

More particularly, in the method according to the present invention, the oxy-combusting step of fuel in the presence of oxygen is carried out in the combustion zone fed by the exhaust effluent and by the combustion stream containing a comburant, simultaneously or separately, or by a mixture of said exhaust effluent and said combustion stream containing a comburant.

Preferably, the temperature in the combustion zone is comprised between 1100°C and 1500 °C, more preferably between 1200°C and 1400°C.

In a further particular embodiment of the present invention, said cooling step comprises a supply of cooling gas at the bottom of each of said shafts or only of the shaft working in the calcining mode.

In a variant of the particular embodiment, according to the present invention, said cooling step comprises a supply of cooling gas at the bottom of the shaft having worked in the preheating mode and before the activation of the inversion means, in order to have each shaft encountering sequentially said preheating mode, a cooling step and then a calcining mode.

In yet a preferred embodiment of the present invention, said cooling gas is air, nitrogen (such as nitrogen from the air separation unit when present) or steam or any mixture thereof and preferably air.

In a particular embodiment of the present invention, said cooling gas, preferably said air, supplied at the bottom of each shaft or of the shaft under calcining mode is ascending, flowing in counter-current through the calcined mineral stones forming a heated cooling gas, preferably a heated air, said heated cooling gas, preferably said heated air being extracted at a level below the connecting channel.

Further, in a particular embodiment, said heated cooling gas, preferably said heated air is extracted outside of the kiln.

Preferably, the temperature of the heated cooling gas, preferably of the heated air, extracted at a level below the connecting channel is comprised between 500°C and 1000°C, more preferably between 700°C and 950°C.

More preferably, the method according to the present invention comprises at least one heat exchange between the heated cooling air, which has been extracted outside the kiln, and said recirculated fraction of gaseous effluent before injection to the shaft in calcining mode.

For example, when the combustion is carried out in presence of a mixture of gaseous effluent and concentrated dioxygen, the mixture is preferably performed in a mixing chamber in fluid communication with the recirculation of exhaust effluent and one dioxygen source and with the combustion zone of the shaft of the kiln in calcining mode. The heat exchange between the heated cooling air, removed from the furnace, and said collected portion of gaseous effluent discharged from the furnace occurs then before or after it is mixed with concentrated dioxygen.

Alternatively or in addition to, in the method according to the present invention, at least one heat exchange between the heated cooling air which has been extracted outside the kiln and said mixing gas

stream, before passing through the series of mixing gas entry means is comprised to provide the increase of temperature to the mixing gas stream.

In a particular embodiment of the present invention, said combustion stream comprising a comburant is O_2-rich gas and said mixing gas stream is O_2-rich mixing gas stream and wherein the total amount of oxygen is calculated by a control system according to the stoichiometric requirement for combustion multiplied by an excess factor supplied by the operator, said amount of oxygen being spread between a first O_2- rich stream and a second O_2-rich stream, said first O_2- rich stream being supplied to the combustion zone of the shaft in calcining mode and said second O_2- rich stream being supplied to the connecting channel.

Preferably, the O2-rich gas and/or the O_2-rich mixing gas stream has an oxygen content comprised between 70 and 100 vol% on dry basis di-oxygen, preferably of at least 80 vol% on dry basis di-oxygen , More particularly of at least 90 vol% on dry basis di-oxygen and most preferably around 93 vol% on dry basis di-oxygen.

It is important to keep the overall oxygen excess for combustion low to keep the final CO_2 in the exhaust effluent sufficiently high (i.e. to not dilute with additional oxygen). In oxyfuel operation, the comburant supplied to the combustion shaft is preferably also high purity oxygen mixed with recycled exhaust effluent. The overall quantity of oxygen supplied to the kiln will be calculated by the control system according to the stoichiometric requirement for combustion, multiplied by an excess factor supplied by the operator (typically between 1.02 and 1.30, preferably between1.03 and 1.2, in particular from 1.04 to 1.17, advantageously from 1.05 to 1.15). This global quantity will then, if relevant, be split between oxygen sent to the shaft in calcining mode, at the level of or in the combustion zone (first O_2- rich stream) and oxygen sent to the connecting channel (second O_2- rich stream).

Concerning the quantity of oxygen possibly supplied to the connecting channel, it is advantageous to heat it up to high temperature,

such as for example above 500°C, preferably above 650°C before injection. This can advantageously be done by said heat exchange aforementioned or by burning a small quantity of fuel (preferably gaseous or liquid, but low-ash solids could also be possible) in the oxygen stream before injection. Another advantage is that high temperature oxygen is a very strong oxidant and would therefore more readily react with the unburnt, leading to more efficient reduction.

In a preferred embodiment, the ratio between the mass flow of the first O_2-rich stream and the mass flow of the second O_2-rich stream is comprised between 4 and 100, preferably 5 and 50, preferably 6 and 20, preferably between 10 and 15 to achieve the best compromise between the most complete combustion possible and the less CO_2 dilution by CO.

Advantageously according to the present invention, said fuel combustion comprises introducing a gaseous, liquid or solid fuel into the shaft in calcining mode and in that, in the case of a solid fuel, said introduction is carried out using a portion of said collected portion of gaseous effluent discharged from the furnace, or using another source of CO_2 as a carrier gas.

More particularly according to the present invention, the O_2-rich gas or the O_2-rich stream is produced in one air separation unit, said separation unit producing from an air entry, a stream of oxygen and a stream of nitrogen.

In a preferred embodiment, the method according to the present invention comprises a step of collecting a portion of the exhaust effluent in a storage unit, preferably after purification for producing a substantially pure CO_2 gas, before or after the step of collecting the exhaust effluent in said buffer, preferably after.

In a preferred embodiment, the exhaust effluent discharged from the shaft in preheating mode has a temperature of 60°C to 160° C. preferably 100° C.

In a variant according to the present invention, said mixing gas stream is exhaust effluent or substantially pure CO_2 gas, optionally fed from the buffer or storage unit. In this embodiment, all the comburant, preferably all the oxygen for combustion was already supplied to the shaft in calcining mode as a comburant mix. The jets are only there to ensure a complete mixing of the incompletely combusted streams with the surrounding remaining comburant mix. Using recycled flue gas ensure no dilution of the flue gas will occur.

In another variant, the mixing gas stream is steam.

In a preferred embodiment according to the present invention, during the step of recirculating said fraction of the gaseous effluent and before the step of injecting the gaseous effluent to the shaft in calcining mode, the gaseous effluent is cooled into a heat exchanger in which water is condensed and discarded forming a cooled and dried gaseous effluent. This is also especially advantageous when the mixing gas stream is steam. The extra steam injected will be removed by the gas cooling step and would therefore not affect the CO_2 concentration.

In yet a preferred embodiment, a portion of the cooled and dried gaseous effluent is further introduced at the top of the shaft in calcining mode at a temperature below 200°C, preferably below 100°C, more preferably between 30 and 50°C, to keep the benefit from the regeneration, with a slightly higher pressure.

Other embodiments of the method according to the present invention are mentioned in the appended claims.

The present invention also relates to a parallel-flow regenerative kiln (PFRK).

Such kiln for implementing the method according to the present invention comprising:

- at least two shafts, interconnected by a connecting channel,
- each of said shafts comprising, in the on or off position,
- at least one fuel supply device,

- at least one supply opening for oxygen-containing oxidant,
- an inlet, for loading carbonate mineral stones, at the top of the shafts,
- an outlet for unloading the calcined material produced, at the bottom of the shafts, a gaseous effluent discharge duct at the top of the shafts, which is connected to a chimney, and
- a supply of cooling air to cool the calcined material produced,

the furnace comprising a system for reversing the operation of the shafts, arranged so that each shaft, in standard mode, operates alternately in calcining mode and in preheating mode, a shaft being in calcining mode for a predetermined time period while at least one other shaft is in preheating mode, and vice-versa, this reversing system therefore controlling said on and off positions, wherein it further comprises

- a recirculation circuit which is arranged between the above-mentioned gaseous effluent discharge duct of the shafts and said oxidant supply openings of the shafts,
- a separating member, capable of collecting a portion of gaseous effluent discharged from the furnace via the duct and introducing it into the recirculation circuit, and
- a source of concentrated dioxygen that is connected with the recirculation circuit in order to supply it with concentrated dioxygen and thereby form an oxidizing mixture, said oxidant supply opening of the shaft in calcining mode being supplied in the on position via said reversing system to ensure fuel combustion,

said connecting channel being provided to transfer combustion fumes from the shaft in calcining mode to at least one shaft in preheating mode, said connecting channel further comprising a series of mixing gas entry means, provided to feed a mixing gas stream from outside of the kiln into the lumen of the connecting channel, said series of mixing gas entry means being operatively connected to a pressurization

device so as to be able to inject a mixing gas stream at high velocity in said connecting channel throughout said series of mixing gas entry means in such a way that a ratio of momentum J between the gas stream and the combustion fumes is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel before reaching the at least one shaft in preheating mode.

As it can be seen, the kiln according to the present invention comprises a cross channel where the gaseous effluent are transferred to the shaft in preheating mode, the cross over channel is provided with a series of mixing gas entry means to feed a mixing gas stream from outside of the kiln into the lumen of the cross over channel. The series of mixing gas entry means is operatively connected to a pressurization device so as to inject said mixing gas stream from the outside of the kiln at high velocity in the said connecting channel to create the momentum needed to reach the momentum ratio J as defined above.

It is foreseen according to the present invention that said series of mixing gas entry means is operatively connected to one or more pressurization device(s) through a distributor or distributors connected to more than one entry means or alternatively that each entry means of said series of mixing gas entry means is connected to its own pressurization device. In the first case, the pressurization device is connected on one side to the distributor and on the other side to a reservoir, a buffer or to a duct of the kiln where the mixing gas stream is a mixing gas stream recovered from the kiln operation.

In the second case, the pressurization device is connected on one side to the entry means and to the other side to a reservoir, a buffer or to a duct of the kiln where the mixing gas stream is a mixing gas stream recovered from the kiln operation.

The kiln according to the invention only has a few structural changes to the exterior of the furnace. Therefore, existing parallel-flow regenerative kilns may be easily arranged to implement a calcining method according to the invention.

According to a preferred embodiment of the present invention, at least one, preferably each mixing gas entry means of said series of mixing gas entry means is chosen between a through-hole or a through-nozzle or a through-distributor allowing to connect a source of mixing gas stream outside of the kiln and said lumen of the connecting channel, optionally by means of additional nozzles.

In a further preferred embodiment of the kiln of the present invention, each mixing gas entry means of said series of mixing gas entry means is disposed along the external wall of the cross-section of the connecting channel, preferably along the ceiling of the external wall of the cross-section.

The gaseous stream entry means each extends across the wall, preferably across the upper external wall of the connecting channel to be able to feed the gaseous stream into the lumen of the connecting channel.

In a further embodiment of the present invention, the crossover channel has a predetermined length L measured along a longitudinal central axis disposed along the cross-channel defined between 2 adjacent shafts and wherein the series of mixing gas entry means is located in a zone having a length l measured along the same longitudinal central axis, said zone being located at a distance L1 of the first shaft along the same longitudinal central axis and at a distance L2 of the second shaft along the same longitudinal central axis, with $L1+L2+l = L$.

Preferably, the length L1 is equal to L2 $\pm$ 20%, preferably L1 = L2.

In a particular embodiment, L1 is defined such as $0,25\ L < L1 < 0.75\ L$.

Optionally, L2 is defined such as $0,25\ L < L2 < 0.75\ L$.

Equally optionally, l is defined such as $0,25\ L < l < 0.75\ L$.

In another embodiment according to the present invention, the mixing gas entry means are located in the peripheral channels of the connecting channel.

In one embodiment of the present invention, the series of mixing gas entry means comprises x row(s) of y mixing gas entry means positioned in series and/or t rows of z mixing gas entry means positioned in parallel, with x, y, z and t being integer higher or equal to 1 and preferably lower than 50, preferably lower than 30.

In a particular embodiment, the mixing gas entry means are disposed according to a regular pattern with y = t and x = z. In another particular embodiment, the mixing gas entry means are disposed in a shifted manner such as for example with for the first raw containing y mixing gas entry means, the second raw containing y-1 mixing gas entry means, the third raw containing y mixing gas entry means and the like.

Preferably the y mixing gas entry means are disposed aligned in series along a line following the external wall of the cross-section of the crossover channel, equally distanced from each other, but not necessarily along the full perimeter of the crossover channel. It is indeed preferred according to some embodiments to have 5, 6, 7, 8 or even 10 entry means located on the upper wall and extending through the wall of the crossover channel to inject the mixing gas stream in the zone where the hot combustion fumes are transferred. Accordingly, the entry means can be located along 1/3, 1/4, 1/5, 1/6 or even 1/8 or 1/10 of the external wall of the cross over channel, preferably in the upper part of the crossover channel.

In a preferred embodiment, wherein each gaseous entry means has an implantation orifice in the connecting channel and one or more mixing gas stream exit, said implantation orifice being positioned in the ceiling of the connecting channel, in the bottom of the connecting channel or in the lateral wall of the connecting channel.

In another preferred embodiment, this later implementation is performed only in the crossover channel, part of the connecting channel.

In a particular embodiment of the present invention, wherein the series of mixing gas entry means comprises x=2n rows of y mixing gas entry means positioned in series, wherein, with respect to a symmetry plan disposed vertically in the middle of the connecting channel, with n rows being located on one side of the symmetry plan and n rows being located on the other side of the symmetry plan, preferably symmetrically at their implantation orifice.

Number n can be for example 1, 2, 3, 4, 5, 6.

Preferably, the installation of gaseous entry means is symmetrical relative to the plane of symmetry of the two shafts.

In another particular embodiment of the present invention, the mixing gas entry means of the n rows have a longitudinal central axis along the flow passing through the mixing gas entry means and centrally, said longitudinal axis of each mixing gas entry means forming an angle with respect to the vertical direction comprised between 15 and 75° in absolute value, injecting co-currently the mixing gas stream with respect to the gaseous effluent or, preferably, injecting counter-currently the mixing gas stream with respect to the gaseous effluent.

Alternatively, the mixing gas entry means of the n rows have a longitudinal central axis along the flow passing through the mixing gas entry means and centrally, said longitudinal axis of each mixing gas entry means forming an angle with respect to the horizontal direction comprised between 15 and 75° in absolute value, injecting co-currently the mixing gas stream with respect to the gaseous effluent or, preferably, injecting counter-currently the mixing gas stream with respect to the gaseous effluent.

In another embodiment according to the present invention, each mixing gas entry means is an elongated hollow body (through distributor), preferably cylindrical hollow body enclosed in an outer tubular wall, said mixing gas entry means having a first end and a second end, opposed to the first end, said first end being protruding in the lumen of the connecting channel and said second end being in fluid communication

with the outside of the connecting channel, said mixing gas entry means extending preferably through the wall of the connecting channel, with said one or more mixing gas stream exit being one or more through holes performed on the outer tubular body provided to establish a fluid communication between the lumen of the elongated hollow body and the connecting channel.

In a particular embodiment, wherein the elongated hollow body is a divided in a first and a second longitudinal sub-cavities, each sub-cavity having a series of exit holes and wherein the series of exit holes of the first sub-cavity is closed when the series of exit holes of the second sub-cavity is open and wherein the series of exit holes of the first sub-cavity is open when the series of exit holes of the second sub-cavity is closed.

In a further other embodiment of the present invention, said connecting channel further comprises a series of obstacles arranged to increase the mixing between said mixing gas stream and said gaseous effluent.

The series of obstacles can contain 1, 2, 3, 4, 5, 6, 7, 8 or even 10 obstacles extending from any part of the internal wall of the cross over-channel. The obstacles can be pillars or baffles and can accordingly be connected at their two ends with the internal wall of the connecting channel or only at one of their ends. The obstacles can be under the form of bars, possibly hollow and cooled, or brick pillars. These obstacles could also be placed in staggered rows.

Other types of obstacles are also contemplated such as, for example a "bluff body" suspended in the middle of the channel.

Preferably, the series of obstacles extends from the internal wall of the connecting channel, more particularly from the upper internal wall. The series of obstacles can be located in a portion having a length l' measured in the direction of the longitudinal central axis of the crossover channel and, said portion being located at a distance L'1 of the first shaft in the direction of said longitudinal central axis and at a distance L'2 of

the second shaft in the direction of said longitudinal central axis, with L'1+L'2+l'= L (Length of the crossover channel).

Preferably, the length L'1 is equal to L'2 ± 20%, and preferably L'2 = L'1.

In a particular embodiment, L'1 is defined such as 0.25 L < L'1 < 0.75 L.

Optionally, L'2 is defined such as 0,25 L < L'2 < 0.75 L.

Equally optionally, l' is defined such as 0,25 L < l' < 0.75 L.

In one embodiment of the present invention, the series of obstacles comprises z' row(s) of t' obstacles positioned in series, with z' and t' being integer equal or higher than 1 and preferably lower than 10.

Preferably the t' obstacles are disposed aligned in series along a line following the internal wall of the cross-section of the connecting channel, equally distanced from each other, but not necessarily along the full internal perimeter of the connecting channel. It is indeed preferred according to some embodiments to have 5, 6, 7, 8 or even 10 obstacles located on the internal wall and extending from the internal wall of the connecting channel to create turbulences in the zone where the hot combustion fumes are transferred. Accordingly, the obstacles can be located along 1/3, ¼, 1/5, 1/6 or even 1/8 or 1/10 of the internal wall of the cross over channel.

In a particular embodiment of the present invention, the series of obstacles comprises z=2a rows of t' obstacles positioned in series, wherein, with respect to a symmetry plan disposed vertically in the middle of the connecting channel, a rows are located on one side of the symmetry plan and a rows are located on the other side of the symmetry plan, preferably symmetrically. Number a is an integer and can be for example 1, 2, 3, 4, 5, 6.

In another particular embodiment, the obstacle of the series of obstacles has a heigh that is comprised between 10 and 75% of the height or diameter of the lumen of the connecting channel.

According to an embodiment of the invention, wherein the shafts have a circular cross-section, in that the connecting channel comprises a crossover channel and the peripheral channels, the cross over channel connecting the peripheral channels arranged around each shaft so as to allow a transfer of gas and in that, below the connecting channel, the shafts are provided with a collector ring connecting with an evacuation element so as to allow heated cooling air to be removed from the furnace.

Advantageously, the circular shafts further comprise, at the bottom, a central collector element connecting with an evacuation element so as to allow heated cooling air to be removed from the furnace, below the connecting channel.

According to another embodiment of the furnace according to the invention, the shafts have a rectangular cross-section, in that a first side of a shaft faces a first side of a neighboring shaft and each shaft comprises a second side that is opposite those facing each other and in that the connecting channel is a crossover channel which directly connects one shaft to the other via their first sides, and in that, below the connecting channel, said first sides and said second sides of the shafts are provided with a collection tunnel connecting with an evacuation element so as to allow heated cooling air to be removed from the furnace..

According to an embodiment of the invention, the furnace comprises, as a dioxygen source for the recirculation circuit, an air separation unit for separating air into dioxygen and dinitrogen. An oxygen tank may also be provided. Advantageously, a heat exchanger supplied with heated cooling air removed from the furnace is mounted on the recirculation circuit to heat the above-mentioned oxidizing mixture before it is supplied to the shaft in calcination mode.

In a preferred embodiment, the kiln according to the present invention comprises a control system provided for, when said combustion fumes comprising a comburant is O_2-rich gas and said mixing gas stream is O_2-rich mixing gas stream, calculating an amount of oxygen in excess

for the step of oxy-combusting the fuel according to the stoichiometric requirement for combustion multiplied by an excess factor supplied by the operator and a spreader provided to spread said amount of oxygen between a first O_2-rich stream and a second O_2-rich stream, said first O_2-rich stream being supplied to the combustion zone of the shaft in calcining mode and said second O_2-rich stream being supplied to the connecting channel.

In still a preferred embodiment, the kiln according to the present invention comprises, downstream or upstream the pressurization means, heating means to heat said mixing gas stream before injection in the connecting channel, said heating means being preferably chosen amongst a heat exchanger, a combustion chamber, electrical heater.

Preferably, wherein said recirculation circuit is connected to at least one buffer unit.

In a particular embodiment of the present invention, in the kiln of the present invention, said recirculation circuit is connected to storage unit provided to store a CO_2-rich gaseous effluent, optionally before or after a buffer unit.

Other features and details of the kiln according to the invention are indicated in the appended claims.

Other particularities of the invention will also result from the non-limiting description given below, with reference to the Figures illustrating the present invention.

FIG. 1 schematically shows a conventional PFRK furnace of circular cross-section.

FIGS. 2, 3 and 4 schematically show several embodiments of the furnace with a circular cross-section according to the invention.

FIG. 5 schematically shows one embodiment of the mixing gas entry means of the furnace according to the present invention.

FIG. 6 schematically shows one embodiment of the mixing gas entry means of the furnace according to the present invention

arranged to ensure a counterflow injection of the mixing gas stream in a kiln with circular or rectangular shaft.

FIGS. 7, 8 and 9 show cross-section views of different embodiments of the furnace according to the invention.

In the figures, identical or similar parts use the same references. Conventionally, the shaft shown on the left is in calcination mode and the shaft shown on the right is in preheating mode. Standard parts, such as loading or unloading equipment, are not shown or they are shown very schematically, in order to not overload the drawings.

As can be seen in FIG. 1 , the PFRK furnace shown is a vertical double-shaft furnace 1, 2, where the fuel is injected alternately in one shaft 1 then in another 2 for approximately 12 minutes with a stop period between cycles of 1 to 2 minutes to reverse the circuits. This is the "reversing" period. Both shafts have a circular cross-section and are provided with peripheral channels 13 which are interconnected by a crossover channel 3. The shafts are divided vertically into three areas, the preheating area A where the carbonate stones is preheated before calcination, the combustion area B where the calcination of the carbonate stones occurs and the cooling area C where the cooling of the calcined material occurs.

When a shaft is in calcination mode, here the shaft 1, a fuel supply device in the form of lances 4 injects a fuel 9 into the shaft, which, in the example shown, is natural gas. The carbonate stones, loaded at the top of the shaft via an inlet 5 in the open position, progressively descends in the shaft. Combustion air is introduced at the top of the shaft via a supply opening 6, which allows for fuel combustion at the outlet of the lances 4 and a decarbonation of the carbonate stones to calcined material 10. The mixing gas stream 11 formed by the combustion and decarbonation descends co-currently to the calcined material and, using the peripheral channel 13, moves into the crossover channel 3. Cooling air is introduced via a supply duct 7 at the bottom of the shaft, counter-currently to the calcined material, to cool it. The heated cooling air 12

introduced in the calcination shaft mixes with the combustion fumes 11 in order to move into the crossover channel 3. The calcined material is unloaded via the outlet 8 into a piece of unloading equipment 24.

When a shaft is in preheating mode, here the shaft 2 , the fuel supply device is closed and the lances 4 are therefore off. The same applies to the inlet 5 for the carbonate stones and to the opening 6 for supplying combustion air. However, the supply duct 7 for the cooling air and the outlet 8 for the calcined material remain in the open position. After heat exchange with the descending calcined material 10, the heated cooling air mixes with the combustion fumes 11 which, from the crossover channel 3, enters the shaft via the peripheral channel 13. The combustion fumes 11 progresses until reaching the top of the shaft where it is discharged from the furnace via a discharge duct 14 and transferred to a chimney 15, possibly after treatment in equipment's such as filters. In the shaft in calcination mode 1, this discharge duct 14 is closed.

The furnace also comprises a reversing system 16, shown schematically. It controls, in a synchronized manner, the operation of the shafts during the reversing time of the shafts, either directly or remotely. It controls the on and off switching of all elements of the furnace in such a way that, in production mode, each shaft operates alternately in calcination mode and in preheating mode.

In some cases, there are three shafts, two in preheating mode and one in combustion.

FIG. 2 is a view of an advantageous furnace according to the present invention. As can be seen, this embodiment comprises separating member 17, capable of collecting a portion of gaseous effluent discharged from the furnace and introducing it into the recirculation circuit 18, and which has been provided on the exterior, on the discharge duct 14. In this circuit, the collected portion of gaseous effluent is advantageously treated in a treatment unit 19, where it may, for example, be filtered and/or dried. An air separation unit 20 separates air supplied by the duct 21 into N2 discharged via the duct 22 and O2 supplied to the

recirculation circuit 18 via the supply duct 23. This circuit 18 then brings the oxidizing mixture formed from the recirculated portion of gaseous effluent and concentrated O2 to the top of each of the shafts at the supply opening 6.

The separating member 17 is continuously in service during combustion, the same as the treatment unit 19 and the air separation unit 20. As has already been seen, the reversing system 16 closes the discharge duct 14 at the top of the shaft in calcination mode. However, at the top of this shaft, it opens the supply opening 6 to allow the oxidizing mixture to be introduced, while it is closed at the top of the shaft in preheating mode.

In addition, the heated cooling air is extracted after contact with the calcined material, by installing a removal system. The shafts 1 and 2 are each provided with a collector ring 25, below the crossover channel 3, which connects with an evacuation element 26 so as to allow heated cooling air to be removed from the furnace. In this way, a portion or all of the combustion air may be extracted, as required, by also extracting a small proportion of combustion fumes. The shafts may further optionally comprise, at the bottom, a central collector element 27 connecting with the evacuation element 26 as to also allow a central removal of the heated cooling air, below the crossover channel 3. Moreover, in order to recover a portion of the energy from the hot air removed by the evacuation element 26, a heat exchange may be provided with the portion of recirculated gaseous effluent using a heat exchanger 36, before or after the mixing thereof with concentrated dioxygen.

In the connecting channel or crossover channel 3, an injection of a fraction of said collected portion of gaseous effluent discharged from the furnace using an injection duct 37 may also be provided. Optionally beforehand, a heat exchange between the heated cooling air removed from the furnace, and this above-mentioned fraction to be injected may occur using a heat exchanger, for example the heat exchanger 36. In the absence thereof, another heater not shown may be provided on the injection duct 37.

Preferably, in the connecting channel or crossover channel 3, the injection of a fraction of said collected portion of gaseous effluent discharged from the furnace using the injection duct 37 also comprises an addition of oxygen by a fluid connection of the injection duct 37 with the supply duct 23.

FIG. 3 is a view of another advantageous furnace according to the present invention. As can be seen, this embodiment is similar to the embodiment of the furnace described in FIG. 2 except that the injection duct 37 is replaced by a system to inject a mixture of fuel and oxygen into the connecting channel or crossover channel 3.

Preferably the system to inject a mixture of fuel and oxygen into the connecting channel or crossover channel 3 comprises :

- a combustion chamber 42,
- a duct 41 in fluid connection with the supply duct 23 and with the combustion chamber 42, the duct 41 being arranged to provide oxygen into the combustion chamber 42,
- a fuel injection duct 40 in fluid connection with the combustion chamber 42, wherein the fuel injection duct 40 is arranged to inject fuel able to heat the oxygen in the combustion chamber 42 in order to provided hot oxygen,
- a duct 43 in fluid connection with the combustion chamber 42 and the series of mixing gas entry means of the connecting channel or crossover channel 3 arranged to inject the mixing gas stream (mixture of fuel and oxygen) at high velocity in such a way that a ratio of momentum J between the gas stream and the combustion fumes is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel.

FIG. 4 is a view of another advantageous furnace according to the present invention. As can be seen, this embodiment is similar to the embodiment of the furnace described in FIG. 2 except that the injection

duct 37 is replaced by a system to inject steam from a steam source 44 into the connecting channel or crossover channel 3 through an injection duct 45.

FIG. 5 shows a section of a part of the furnace according to the present invention centered on the crossover channel 3 showing one mixing gas entry means 46 of the series of mixing gas entry means fluidly connected to a circuit arranged to provide a fluid connection between each mixing gas entry means 46 and the gaseous effluent duct, injection duct, 37 or 43 or 45, said circuit comprising:

- a pressurization device 47 fluidly connected to said gaseous effluent duct 37 or 43 or 45,
- a valve system 48 fluidly connecting the pressurization device 47 and each mixing gas entry means 46.

In the embodiment of the furnace according to the invention illustrated in FIGS. 5 and 6, each mixing gas entry means 46 of said series of mixing gas entry means comprises one end being a series of nozzle 50 and/or a series of hole 51.

Preferably, the valve system 48 is a distribution valve or at least two separate valves.

In FIG. 5 and FIG. 6A, the direction of the arrows 53 in the crossover channel 3 indicates the direction of the combustion fumes 11. In FIG. 5, the mixing gas stream 54 is injected in counter-current with respect to the combustion fumes, i.e. the nozzle 50 injects said mixing gas stream in the combustion fumes through the exit hole 51 when the shaft on the left 1 is in calcining mode and the nozzle 50' is not open. When the shaft on the right 2 is in calcining mode, then the nozzle 51 is closed and the nozzle 51' is open and inject then in counter-current the mixing gas stream 54 in the combustion fumes 53. The turbulence in the flow of the combustion fumes is increased by means of a series of obstacles 55 present in the crossover channel. Such turbulence in the flow of the combustion fumes contributes to increase the oxidation of the CO.

In FIG. 6A, the mixing gas entry means 46 are located in a transversal channel provided in the middle of the crossover channel. In the transversal channel, the mixing gas entry means 46, illustrated in details in the FIG 6B is introduced. The mixing gas entry means is a distributor (elongated hollow body) having holes on one side 51 of the external wall and on the opposite side 51'. The external wall is substantially tubular with a circular cross-section but can be also tubular with a rectangular cross-section and is forming a cavity into which the mixing gas stream is injected. The cavity is divided in two portions with an internal wall, defining then 2 sub-cavities. Holes 51 are provided in the external tubular wall of the first sub-cavity and holes 51' are provided in the external tubular wall of the second sub-cavity. The holes 51, 51'are provided to exit the mixing gas stream in the crossover channel. The lumens of the mixing gas entry means (the two sub-cavities) are fluidly connected to any sources of mixing gas stream, depending on the embodiment. In Fig 6A, the shaft on the left is in calcining mode and mixing gas stream the mixing gas stream is directed only to the holes 51, in counter-current to the fumes flow53 in the crossover channel. In FIG. 6B, the direction of the arrows indicates the direction of the mixing gas stream when the shaft on the left is in calcining mode. In this embodiment, the distributor valves 48 send the mixing gas stream to the holes 51 and no gas is sent to the holes 51'.

In FIG. 7, the shafts 1 and 2 of the furnace are on either side of the crossover channel 3 wherein openings 54 are located in a plane that is equally distance from shafts 1 and 2 and perpendicular to the longitudinal axis having a length L along the crossover channel 3. The shafts have either a circular cross-section (FIG. 7A) or a rectangular cross-section (FIG. 7B). The crossover channel has a predetermined length L measured along a longitudinal central axis disposed along the cross-channel defined between shafts 1 and 2 and wherein the series of mixing gas entry means is located in a zone having a length l measured along the same longitudinal central axis, said zone being located at a distance L1 of the first shaft along the same longitudinal central axis and at a

distance L2 of the second shaft along the same longitudinal central axis, with L1+L2+I = L.

As shown in FIG. 8, which shows a cross-section view of a furnace according to the invention, the injection of the gases containing additional air can be carried out not only through the openings 54 provided in the crossover channel, but also by the openings 57 provided in the peripheral channels 13.

FIG. 9 shows a cross-section view in such an embodiment of the furnace according to the invention comprising 3 shafts 1, 2 and 58 interconnected by 3 crossover channels 3 , 59 and 60. The shafts 2 and 58 are in preheating mode while the shaft 1 is in calcination mode and so on.

Obviously, the present invention is not limited to the disclosed embodiment and several modifications may be provided without being outside the scope of the appended claims.

CLAIMS

1. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln having at least two shafts (1, 2) interconnected by a connecting channel (13, 3), comprising, in standard operation,

- loading carbonate mineral stones at the top of each shaft,
- preheating these loaded stones in a preheating zone (A),
- calcining these preheated stones in a calcination zone (B) with production of a decarbonated calcined material,
- cooling the calcined material with cooling gas in a cooling zone (C), with formation of heated cooling gas by heat exchange,
- discharging the calcined material from the bottom of the shafts,
- exhausting a gaseous effluent from the kiln,
- each shaft alternately working in a calcining mode and in a preheating mode, one shaft working in a calcination mode during a predetermined time period during which at least another shaft works in a preheating mode, and inversely after activation of the inversion means,
- the calcining mode comprising :
  - in the presence of said preheated carbonate mineral stones descending into said shaft, oxy-combusting fuel in the presence of oxygen so as to obtain said calcination of said stones in said combustion zone (B), and the decarbonation thereof into calcined material (10) with the release of combustion fumes (11) descending co-currently in the shaft in calcination mode, and
  - through said connecting channel (3, 13), a passage of said combustion fumes toward the at least one shaft working in a preheating mode, where a mixing gas stream (54) is injected through a series of mixing gas

entry means (46) at high velocity in such a way that a ratio of momentum J between the each gas stream and the combustion fumes (11) is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel

- said preheating mode comprising :

  - said preheating step of the loaded carbonate mineral stones by heat exchange with said combustion fumes (11) depleted in CO coming from the connecting channel (3, 13), which is ascending and flows in counter-current through the loaded carbonate mineral stones (10), and
  - said exhausting step of said combustion fumes depleted in CO as gaseous effluent at the top of said at least one shaft in preheating mode,

said method further comprising

- recirculating a fraction of the gaseous effluent exhausted from the top of said at least one shaft in preheating mode,
- injecting the gaseous effluent, exhausted from the top of said at least one shaft in preheating mode, to the shaft in calcining mode, either under the form of a comburant mixture or with an injection of a combustion stream containing a comburant, for said step of oxy-combusting the fuel.

2. Method according to claim 1, wherein said ratio of momentum J is higher or equal to 2, more preferably higher or equal to 4, more preferably higher or equal to 5, more preferably higher than or equal to 6, in particular higher than or equal to 7, more particularly higher than or equal to 8, even higher than or equal to 9 or higher than or equal to 10.

3. Method according to claim 1 or claim 2, wherein said mixing gas stream (54) is chosen in the group consisting of a CO_2-rich mixing gas stream, a O_2-rich mixing gas stream, a steam mixing gas stream

or a mixture thereof, to be compatible with oxyfuel or oxy-combustion CO_2 concentration.

4. Method according to any of the preceding claims, wherein said mixing gas stream (54) is pressurized before passing through the series of mixing gas entry means (46) to reach a differential pressure between said mixing gas stream and the gas inside the connecting channel comprised between 100 mbar and 10 000 mbar.

5. Method according to any of the preceding claims wherein said mixing gas stream (54) is heated before passing the series of mixing gas entry means (46) to a temperature comprised between 10 °C and 1000 °C, more preferably between 50°C and 1000°C, most preferably between 75°C and 800°C, as the increase of temperature will increase volume and therefore the velocity.

6. Method according to any of the preceding claims, wherein the exhaust effluent is partially or fully collected in at least one buffer after said exhausting step.

7. Method according to any of the preceding claims, wherein said combustion stream containing a comburant is chosen amongst O_2-rich gas mixture, in particular pure oxygen, a steam-based gas mixture containing oxygen or their mixture.

8. Method according to any of the preceding claims, wherein oxygen is introduced in the kiln at one or more locations to provide a total amount of oxygen introduced in the kiln higher than the amount required for a stoichiometric combustion for the oxy-combustion of fuel in presence of oxygen in excess, and is preferably introduced at an excess from 2 to 30%, preferably from 3 to 20 %, in particular from 4 to 17%, advantageously from 5 to 15 % in volume with respect to the stoichiometric need of the combustion reaction.

9. Method according to any of the preceding claims, wherein said oxy-combusting step of fuel in the presence of oxygen is carried out in the combustion zone (B) fed by the exhaust effluent and by the

combustion stream containing a comburant, simultaneously or separately, or by a mixture of said exhaust effluent and said combustion stream containing a comburant.

10. Method according to any of the preceding claims, wherein said cooling step comprises a supply of cooling gas at the bottom of each of said shafts or only of the shaft working in the calcining mode.

11. Method according to any of the claims 1 to 9, wherein said cooling step comprises a supply of cooling gas at the bottom of the shaft having worked in the preheating mode and before the activation of the inversion means, in order to have each shaft encountering sequentially said preheating mode, a cooling step and then a calcining mode.

12. Method according to any of the preceding claims, wherein said cooling gas is air, nitrogen (such as nitrogen from the air separation unit when present) or steam or any mixture thereof and preferably air.

13. Method according to any of the preceding claims, wherein said cooling gas, preferably said air, supplied at the bottom of each shaft or of the shaft under calcining mode is ascending, flowing in counter-current through the calcined mineral stones forming a heated cooling gas, preferably a heated air, said heated cooling gas, preferably said heated air being extracted at a level below the connecting channel.

14. Method according to claim 13, wherein said heated cooling gas, preferably said heated air is extracted outside of the kiln.

15. Method according to claim 13 or claim 14, further comprising at least one heat exchange (36) between the heated cooling air, which has been extracted outside the kiln, and said recirculated fraction of gaseous effluent before injection to the shaft in calcining mode.

16. Method according to any of the claims 13 to 15, further comprising at least one heat exchange between the heated cooling air which has been extracted outside the kiln and said mixing gas stream, before passing through the series of mixing gas entry means (46).

17. Method according to any of the claims 3 to 16, wherein said combustion stream comprising a comburant is O_2-rich gas and said mixing gas stream is O_2-rich mixing gas stream and wherein the total amount of oxygen is calculated by a control system according to the stoichiometric requirement for combustion multiplied by an excess factor supplied by the operator, said amount of oxygen being spread between a first O_2-rich stream and a second O_2-rich stream, said first O_2-rich stream being supplied to the combustion zone of the shaft in calcining mode and said second O_2-rich stream being supplied to the connecting channel.

18. Method according to claim 17, wherein the ratio between the first O_2-rich stream and the second O_2-rich stream is comprised between 4 and 100 to achieve the best compromise between the most complete combustion possible and the less CO_2 dilution by CO.

19. Method according to any of the preceding claims, wherein said fuel combustion comprises introducing a gaseous, liquid or solid fuel into the shaft in calcining mode and in that, in the case of a solid fuel, said introduction is carried out using a portion of said collected portion of gaseous effluent discharged from the kiln, or using another source of CO_2 as a carrier gas.

20. Method according to any of the previous claims, wherein the O_2-rich gas or the O_2-rich stream is produced in one air separation unit, said separation unit producing from an air entry, a stream of oxygen and a stream of nitrogen.

21. Method according to any of the preceding claims, further comprising a step of collecting a portion of the exhaust effluent in a storage unit, preferably after purification for producing a substantially pure CO_2 gas, before or after the step of collecting the exhaust effluent in said buffer, preferably after.

22. Method according to any of the preceding claims, wherein said mixing gas stream is exhaust effluent or substantially pure CO_2 gas, optionally fed from the storage unit and/or the buffer.

23. Method according to any of the preceding claims, wherein during the step of recirculating said fraction of the gaseous effluent and before the step of injecting the gaseous effluent to the shaft in calcining mode, the gaseous effluent is cooled into a heat exchanger in which water is condensed and discarded forming a cooled and dried gaseous effluent.

24. Method according to claim 23, wherein a portion of the cooled and dried gaseous effluent is further introduced at the top of the shaft in calcining mode at a temperature below 200°C, preferably below 100°C, more preferably between 30 and 50°C.

25. Parallel-flow regenerative kiln for implementing the method according to anyone of the preceding claims, comprising

- at least two shafts (1, 2), interconnected by a connecting channel (3, 13),
- each of said shafts (1, 2) comprising, in the on or off position,
- at least one fuel supply device (4),
- at least one supply opening for oxygen-containing oxidant (23),
- an inlet (6), for loading carbonate mineral stones, at the top of the shafts,
- an outlet (8) for unloading the calcined material produced, at the bottom of the shafts, a gaseous effluent discharge duct at the top of the shafts, which is connected to a chimney (15), and
- a supply of cooling gas (7) to cool the calcined material produced,

the furnace comprising a system (16) for reversing the operation of the shafts, arranged so that each shaft, in standard mode, operates alternately in calcining mode and in preheating mode, a shaft being in calcining mode for a predetermined time period while at least one other shaft is in preheating mode, and vice-versa, this reversing system (16) therefore controlling said on and off positions, wherein it further comprises

- a recirculation circuit (18) which is arranged between the above-mentioned gaseous effluent discharge duct of the shafts and said oxidant supply openings of the shafts (6),
- a separating member (17), capable of collecting a portion of gaseous effluent discharged from the furnace via the duct and introducing it into the recirculation circuit (18), and
- a source of concentrated dioxygen (20) that is connected with the recirculation circuit (18) in order to supply it with concentrated dioxygen and thereby form an oxidizing mixture, said oxidant supply opening of the shaft in calcining mode being supplied in the on position via said reversing system (16) to ensure fuel combustion,
- said connecting channel (3, 13) being provided to transfer combustion fumes from the shaft in calcining mode to at least one shaft in preheating mode, said connecting channel (3, 13) further comprising a series of mixing gas entry means (46), provided to feed a mixing gas stream from outside of the kiln into the lumen of the connecting channel (3, 13), said series of mixing gas entry means (46) being operatively connected to a pressurization device (47) so as to be able to inject a mixing gas stream at high velocity in said connecting channel (3, 13) throughout said series of mixing gas entry means (46) in such a way that a ratio of momentum J between the gas stream and the combustion fumes is higher than 1, forming combustion fumes depleted in CO exiting the connecting channel (3, 13) before reaching the at least one shaft in preheating mode.

26. Parallel-flow regenerative kiln according to claim 25, wherein at least one, preferably each mixing gas entry means (46) of said series of mixing gas entry means is chosen between a through-hole (51,

51') or a through-nozzle (50) or a through-distributor allowing to connect a source of mixing gas stream outside of the kiln and said lumen of the connecting channel (3, 13), optionally by means of additional nozzles.

27. Parallel-flow regenerative kiln according to claim 25 or claim 26, wherein each mixing gas entry means (46) of said series of mixing gas entry means is disposed along the external wall of the cross-section of the connecting channel (3, 13), more particularly in the ceiling of the connecting channel (3, 13), in the bottom of the connecting channel (3, 13)or in the lateral wall of the connecting channel (3, 13), preferably along the ceiling of the external wall of the cross-section.

28. Parallel-flow regenerative kiln according to any of the claims 25 to 27, wherein the connecting channel (3, 13) comprises a crossover channel (3) having a predetermined length L measured along a longitudinal central axis disposed along the cross-channel (3) defined between 2 adjacent shafts (1, 2) and wherein the series of mixing gas entry means (46) is located in a zone having a length l measured along the same longitudinal central axis, said zone being located at a distance L1 of the first shaft along the same longitudinal central axis and at a distance L2 of the second shaft along the same longitudinal central axis, with L1+L2+l = L.

29. Parallel-flow regenerative kiln according to claim 28, wherein the length L1 is equal to L2 + 20%, preferably L1=L2.

30. Parallel-flow regenerative kiln according to claim 28, wherein 0,25 L < L1 < 0.75 L.

31. Parallel-flow regenerative kiln according to claim 28, wherein 0,25 L < L2 < 0.75 L.

32. Parallel-flow regenerative kiln according to claim 28, wherein 0,25 L < l < 0.75 L.

33. Parallel-flow regenerative kiln according to any of the claims 25 to 32, wherein the series of mixing gas entry means (46) comprises x row(s) of y mixing gas entry means positioned in series and/or t rows of z mixing gas entry means positioned in parallel.

34. Parallel-flow regenerative kiln according to any of the claims 25 to 33, wherein each gaseous entry means (46) has an implantation orifice in the connecting channel and one or more mixing gas stream exit, said implantation orifice being positioned in the ceiling of the connecting channel, in the bottom of the connecting channel or in the lateral wall of the connecting channel.

35. Parallel-flow regenerative kiln according to any of the claims 25 to 34, wherein the series of mixing gas entry means (46) comprises x=2n rows of y mixing gas entry means positioned in series, wherein, with respect to a symmetry plan disposed vertically in the middle of the connecting channel (3, 13), with n rows being located on one side of the symmetry plan and n rows being located on the other side of the symmetry plan, preferably symmetrically at their implantation orifice.

36. Parallel-flow regenerative kiln according to claim 35, wherein the mixing gas entry means (46) of the n rows have a longitudinal central axis along the flow passing through the mixing gas entry means and centrally, said longitudinal axis of each mixing gas entry means forming an angle with respect to the vertical direction comprised between 15 and 75° in absolute value, injecting co-currently the mixing gas stream with respect to the combustion fumes or injection counter-currently the mixing gas stream with respect to the combustion fumes.

37. Parallel-flow regenerative kiln according to any of the claims 25 to 36, wherein each mixing gas entry means (46) is an elongated hollow body, preferably cylindrical hollow body enclosed in an outer tubular wall, said mixing gas entry means (46) having a first end and a second end, opposed to the first end, said first end being protruding in the lumen of the connecting channel (3, 13) and said second end being in fluid communication with the outside of the connecting channel (3, 13), said mixing gas entry means (46) extending preferably through the wall of the connecting channel (3, 13), with said one or more mixing gas stream exit being one or more through holes (51, 51') performed on the outer

tubular body provided to establish a fluid communication between the lumen of the elongated hollow body and the connecting channel (3, 13).

38. Parallel-flow regenerative kiln according to claim 37, wherein the elongated hollow body is a divided in a first and a second longitudinal sub-cavities, each sub-cavity having a series of exit holes and wherein the series of exit holes of the first sub-cavity is closed when the series of exit holes of the second sub-cavity is open and wherein the series of exit holes of the first sub-cavity is open when the series of exit holes of the second sub-cavity is closed.

39. Parallel-flow regenerative kiln according to any of the claims 25 to 38, wherein said connecting channel further comprises a series of obstacles (55) arranged to increase the mixing between said mixing gas stream and said combustion fumes.

40. Parallel-flow regenerative kiln according to any of the claims 25 to 39, comprising a control system provided for, when said combustion fumes comprising a comburant is O_2-rich gas and said mixing gas stream is O_2-rich mixing gas stream, calculating a total amount of oxygen according to the stoichiometric requirement for combustion multiplied by an excess factor supplied by the operator and a spreader provided to spread said amount of oxygen between a first O_2-rich stream and a second O_2-rich stream, said first O_2-rich stream being supplied to the combustion zone of the shaft in calcining mode and said second O_2-rich stream being supplied to the connecting channel.

41. Parallel-flow regenerative kiln according to any of the claims 25 to 40, further comprising, downstream or upstream the pressurization means (47), heating means to heat said mixing gas stream before injection in the connecting channel (3, 13), said heating means being preferably chosen amongst a heat exchanger, a combustion chamber, electrical heater.

42. Parallel-flow regenerative kiln according to any one of claims 25 to 41, wherein the shafts have a circular cross-section, wherein said connecting channel comprises a crossover channel (3) and the

peripheral channels (13), the cross over channel (3) connecting the peripheral channels (13) arranged around each shaft (1, 2) so as to allow a transfer of gas and wherein, below the connecting channel (3, 13), the shafts (1, 2) are provided with a collector ring (25) connecting with an evacuation element (26) so as to allow heated cooling air to be removed from the furnace.

43. Parallel-flow regenerative kiln according to any one of claims 25 to 42, wherein the circular shafts further comprise, at the bottom, a central collector element (27) connecting with an evacuation element (26) so as to allow heated cooling air to be removed from the furnace, below the connecting channel.

44. Parallel-flow regenerative kiln according to any one of claims 25 to 43, wherein the shafts have a rectangular cross-section, in that a first side of a shaft faces a first side of a neighboring shaft and each shaft comprises a second side that is opposite those facing each other and in that the connecting channel is a crossover channel (3) which directly connects one shaft to the other via their first sides, and in that, below the connecting channel (3), said first sides and said second sides of the shafts are provided with a collection tunnel (25) connecting with an evacuation element (26) so as to allow heated cooling air to be removed from the furnace.

45. Parallel-flow regenerative kiln according to any one of claims 25 to 44, wherein the furnace comprises, as a dioxygen source for the recirculation circuit (18), a unit (20) for separating air into dioxygen and dinitrogen.

46. Parallel-flow regenerative kiln according to any one of claims 25 to 45, wherein a heat exchanger (36) supplied with heated cooling air removed from the furnace, is mounted on the recirculation circuit (18).

47. Parallel-flow regenerative kiln according to any one of claims 25 to 46, wherein it comprises equipment for unloading calcined material that is resistant to temperatures greater than 100° C.

48. Parallel-flow regenerative kiln according to any of the claims 25 to 47, wherein said recirculation circuit (18) is connected to at least one buffer unit.

49. Parallel-flow regenerative kiln according to any of the claims 25 to 48, wherein said recirculation circuit (18) is connected to storage unit provided to store a CO_2-rich gaseous effluent, optionally before or after a buffer unit.

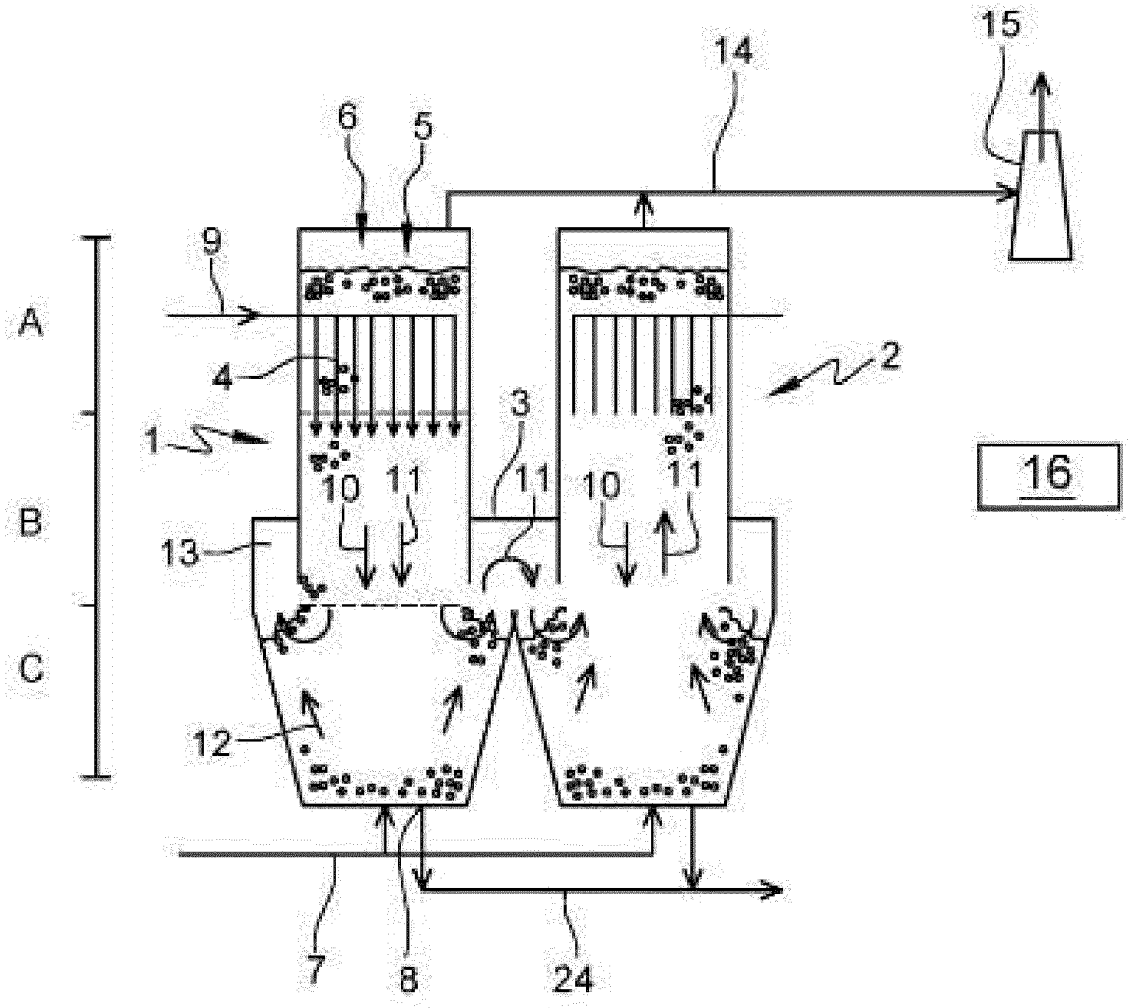


FIG. 1

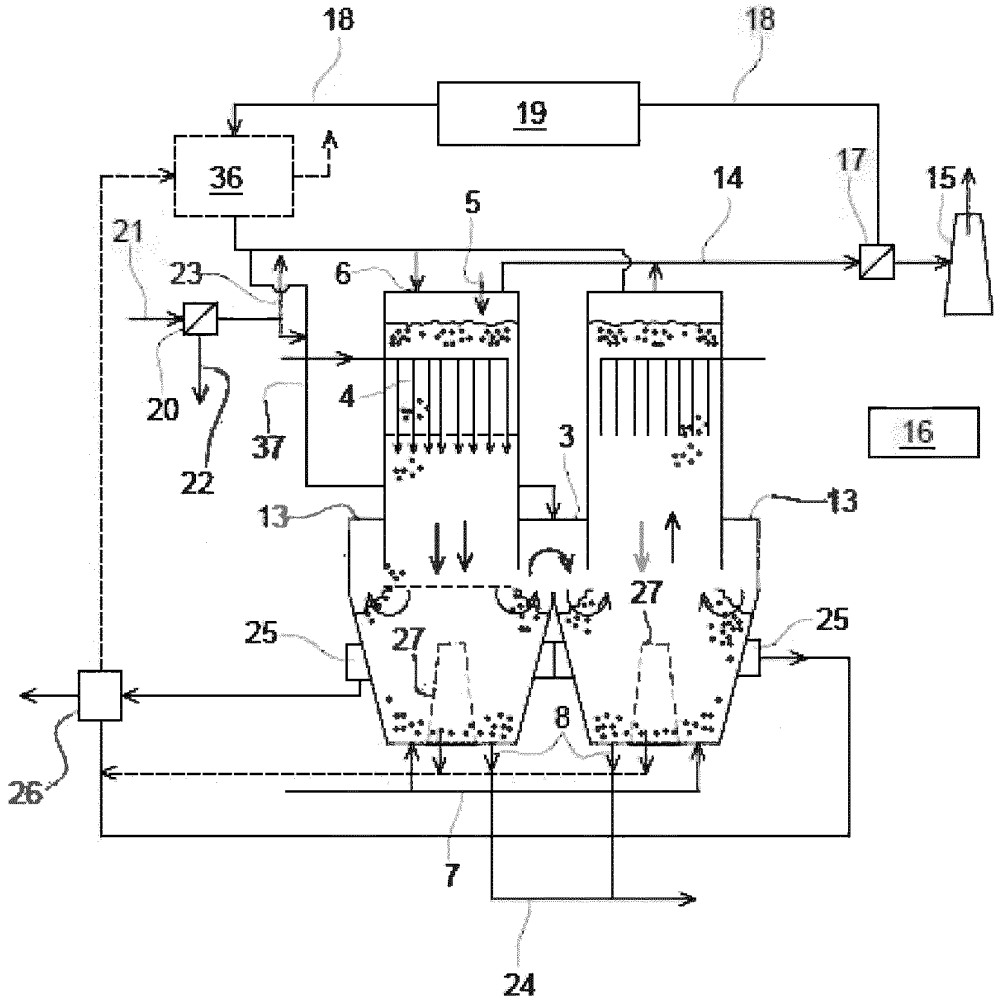


FIG. 2

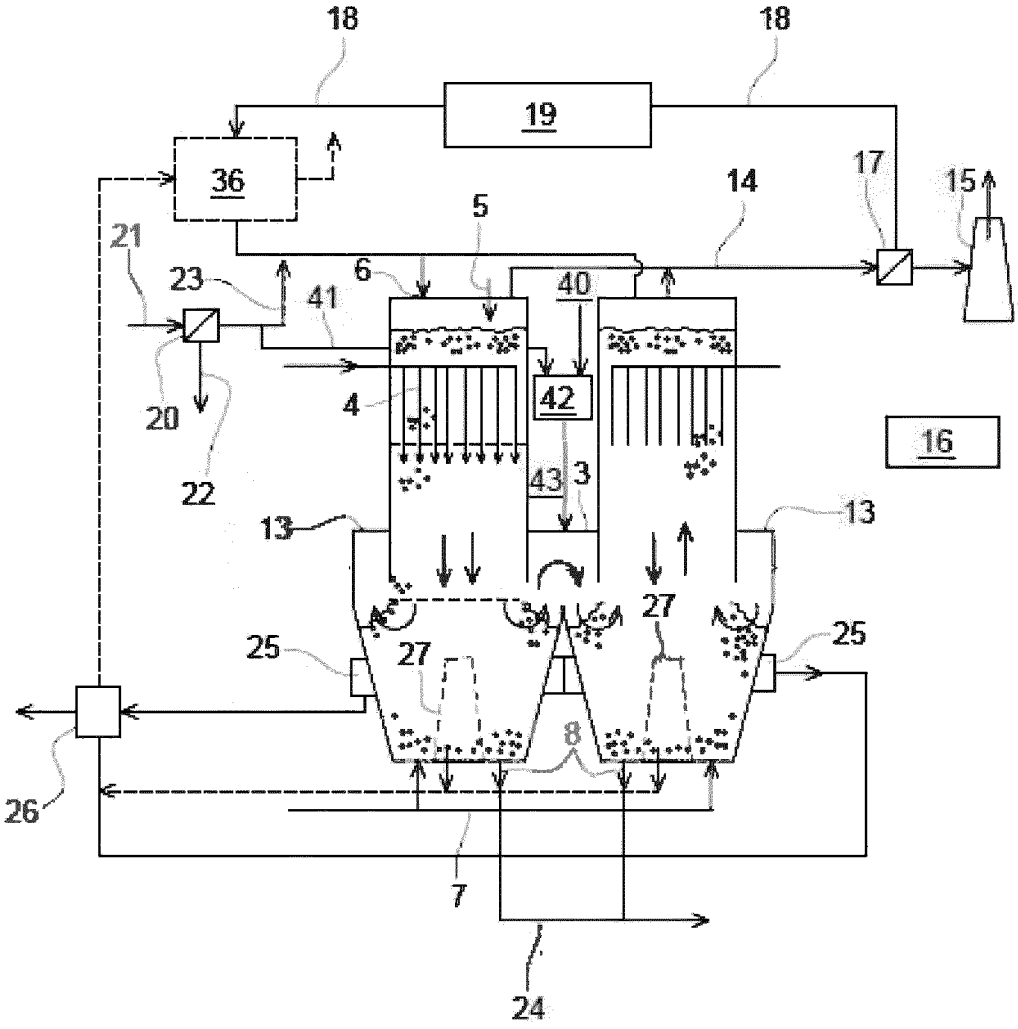

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FIG. 3

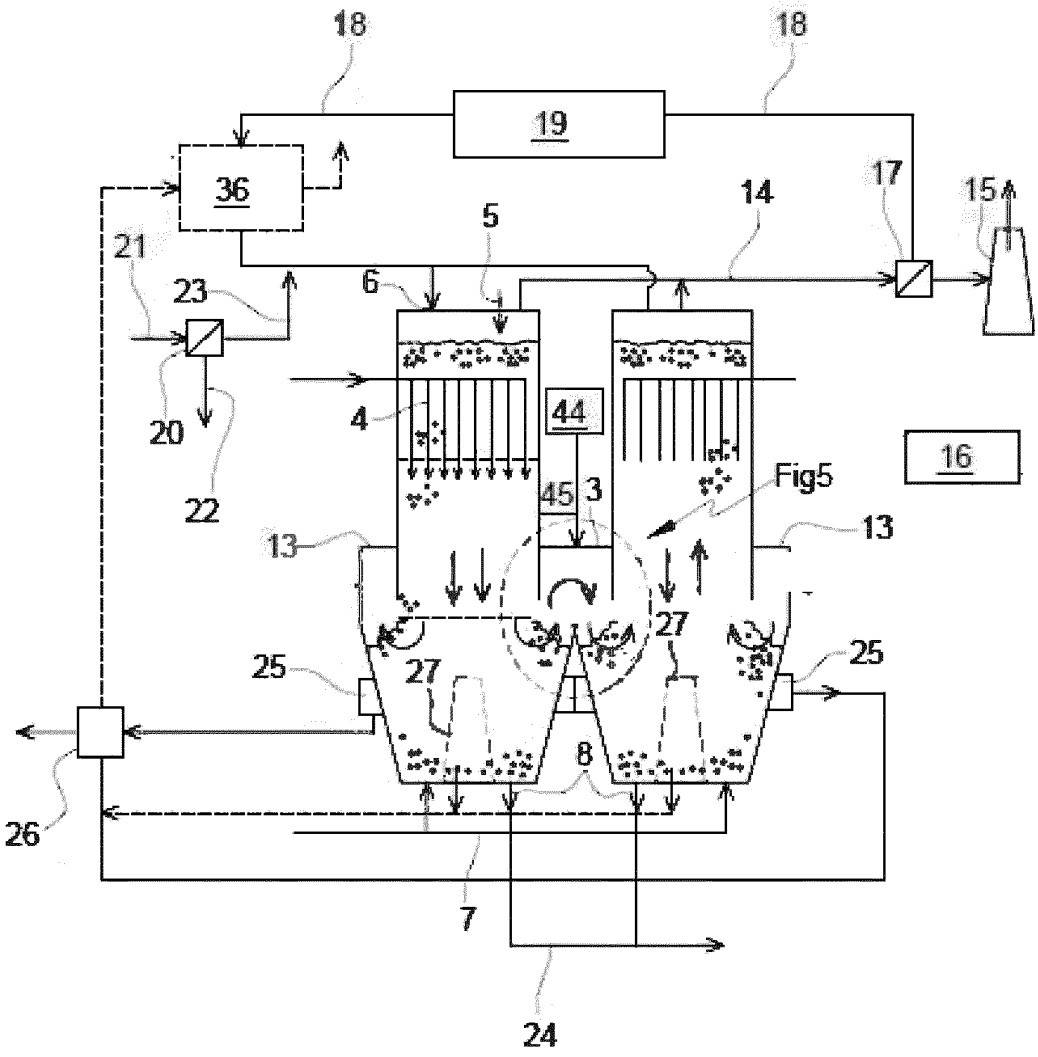

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FIG. 4

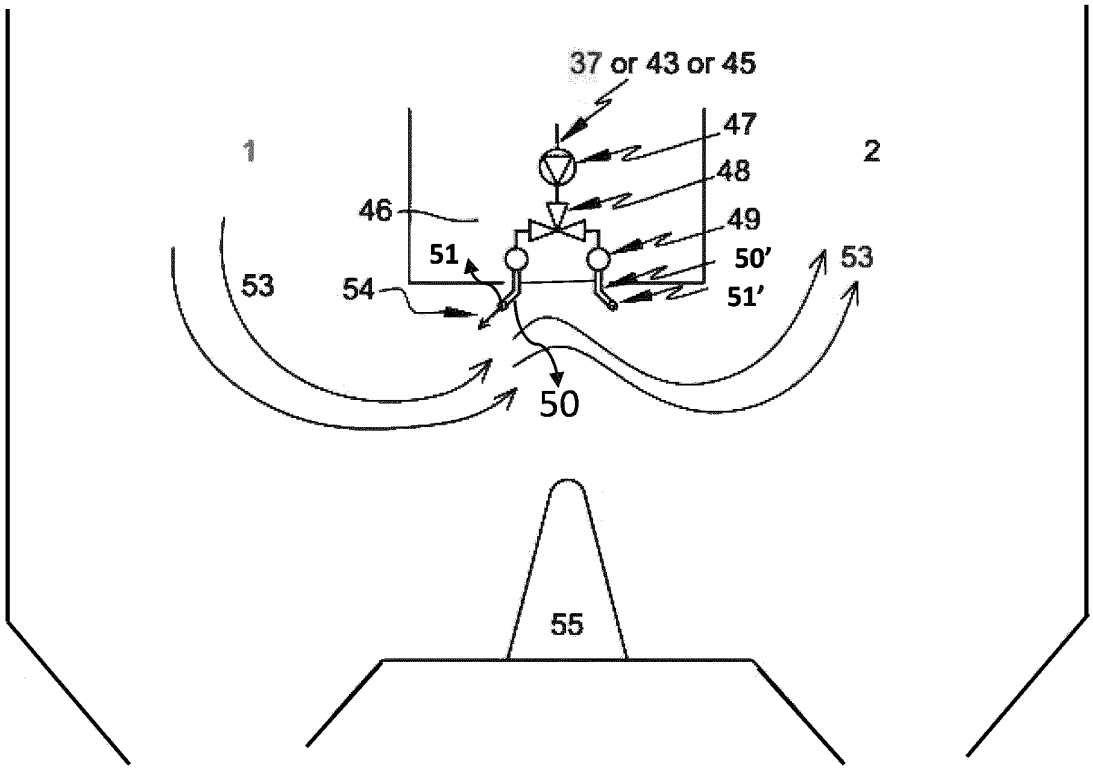


FIG. 5

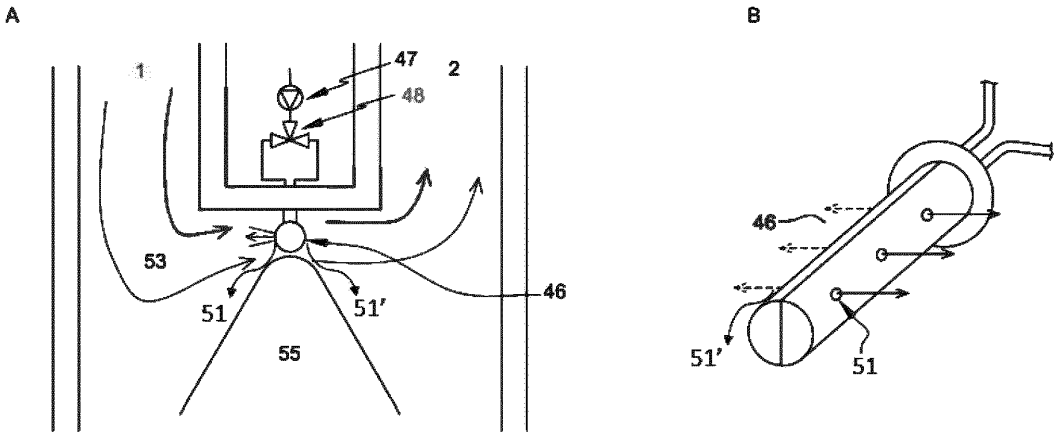


FIG. 6

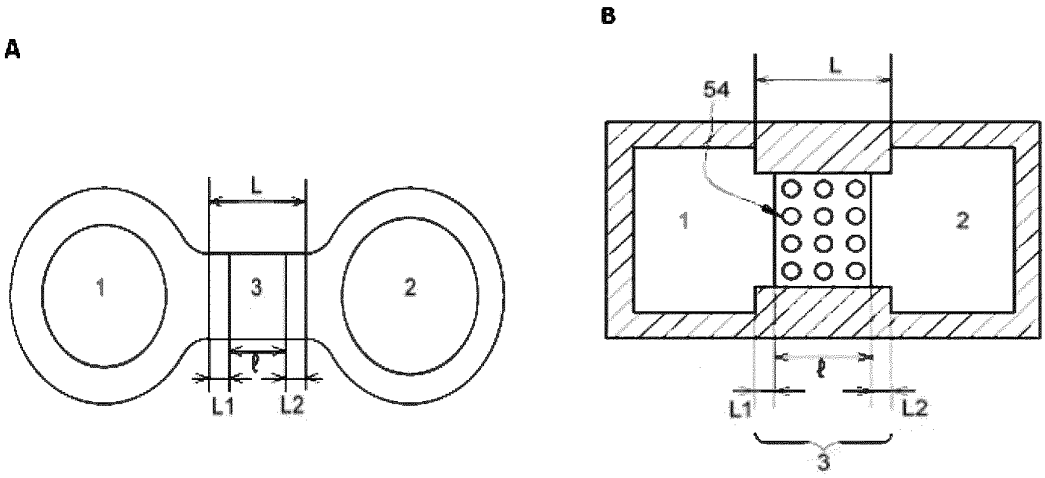


FIG. 7

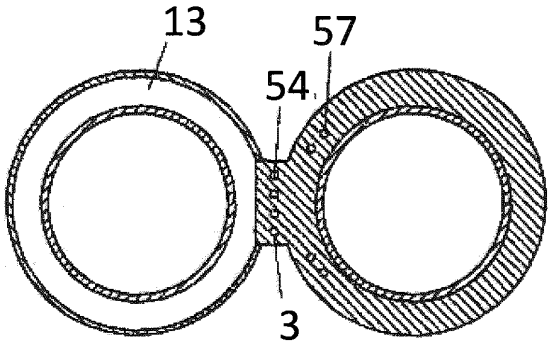


FIG. 8

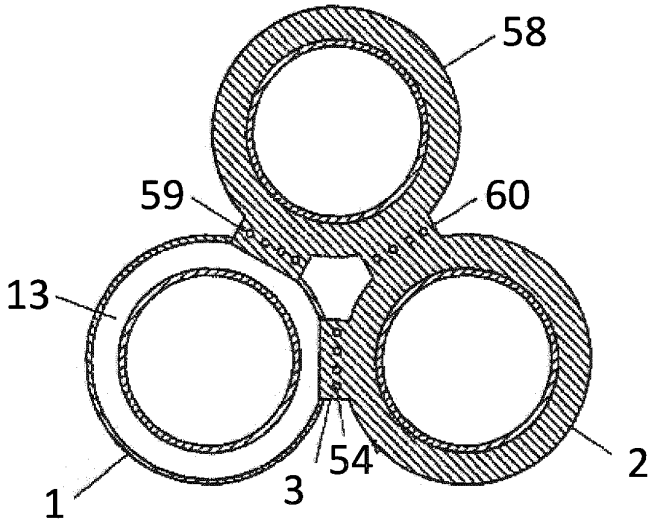


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/058011

A. CLASSIFICATION OF SUBJECT MATTER

INV. F27B1/00 C04B2/12 F27B1/02 F27B1/26 F27D17/00
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)

F27B C04B F27D

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.
X	WO 2022/002869 A1 (LHOIST RECH ET DEVELOPPEMENT SA [BE]) 6 January 2022 (2022-01-06) figure 4 -----	1-49
X	DE 10 2021 204176 A1 (MAERZ OFENBAU [CH]; THYSSENKRUPP AG [DE] ET AL.) 27 October 2022 (2022-10-27) figure 2a -----	1-49

☐ 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
13 December 2024	08/01/2025

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/058011

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