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

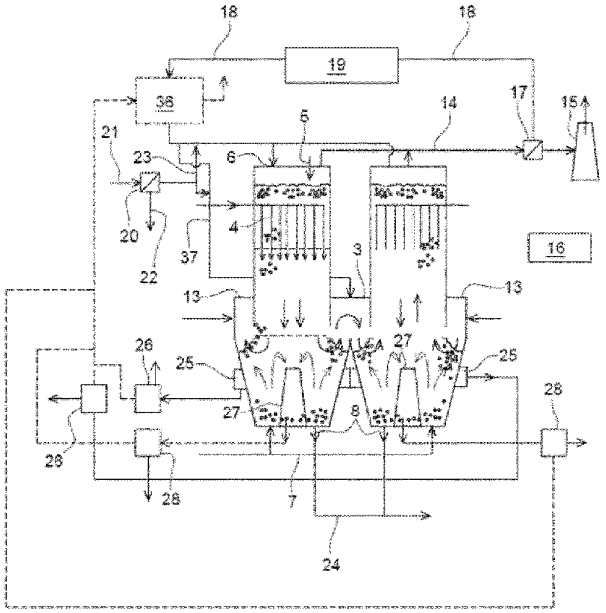



Fig 2

(57) **Abstract:** Method and kiln for calcining carbonate mineral stones in a parallel flow regenerative kiln (PFRK) in oxy-combustion conditions, with improved extraction of cooling gas.

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# « Method and kiln for calcining carbonate mineral stones in a parallel flow regenerative kiln (PFRK)»

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 median 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.

By the terms circular shaft according to the present invention, it is meant a shaft having a substantially circular cross-section, a substantially oval cross-section or any kind of section having more than 4 angles like polygons having for example 5, 6, 8, 10, 12 sides).

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.

The calcined mineral according to the present patent application is typically a calcium-magnesium oxide, also known as quicklime, when containing a low amount of magnesium and dolime 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 gas 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 gas. 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 (calcining shaft) and the shaft(s) wherein the flue gas is drawn through the stones works according to a preheating mode (preheating shaft). 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 gas 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 an exhaust effluent from the kiln,
- each shaft alternately working in a calcining mode and in a preheating mode, one shaft working in a calcining mode during a predetermined time period during which at least another shaft works in a preheating mode, and inversely,
- the calcining mode comprising :

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 exhaust 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 an exhaust effluent being released at the top of the kiln 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 expensive 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 kiln 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 .

Alternatively, one may consider increasing the $CO_2$ concentration in the exhaust effluent.

In this respect, to be able to capture the $CO_2$ emitted in a PFRK kiln, operating PFRK in oxy-combustion seems to be a promising solution, since the exhaust effluent will have a higher $CO_2$ concentration. An example of operation of PFRK in oxy-combustion has been proposed in 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 kiln 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 kiln 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 kiln 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 kiln working in oxy-combustion, the exhaust effluent should be as concentrated in $CO_2$ as possible. Accordingly, there has been some proposals to produce concentrated exhaust gas. One proposal that was discussed above is to replace the cooling air by exhaust effluent such as disclosed in CN10500081 and in JP2002060254. Other proposals are to isolate the cooling air from the exhaust 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 effluent concentrated in $CO_2$ and the cooling air.

As it can be understood, the isolation of cooling air or its replacement to avoid $CO_2$ dilution is a key challenge in the oxyfuel operation of a kiln. However, the replacement of cooling air by another cooling gas is not without impact on the process. Indeed, it can have an impact on the quality of the produced calcined stones or on the CO2 concentration or even requiring additional devices.

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 concentrate and improve the capture the $CO_2$ present in the exhaust effluents emitted by the kiln at a level that enhances its value industrially.

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 decarbonate 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 an exhaust effluent from the kiln,
- each shaft alternately working in a calcining mode and in a preheating mode, one shaft working in a calcining 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 calcining mode, and
  - through said connecting channel, a passage of said combustion fumes 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 combustion fumes 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 as exhaust effluent at the top of said at least one shaft in preheating mode,

said method further comprises

- recirculating a fraction of the exhaust effluent exhausted from the top of said at least one shaft in preheating mode,
- injecting the exhaust effluent, exhausted from the top of said at least one shaft in preheating mode, at least partially 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, said comburant being preferably $O_2$-rich gas
- extracting said heated cooling gas outside of said kiln,

characterized in that during said extracting step of the heated cooling gas outside of the kiln, the heated cooling gas is extracted from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through a collector peripheral ring in fluid connection with the cooling zone, at a level located below the connecting channel and from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through a central collector element in fluid communication with said cooling zone and the heated cooling gas is extracted from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through a collector peripheral ring in fluid connection with the cooling zone, at a level located below the connecting channel and from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through a central collector element in fluid communication with said cooling zone.

As it can be seen, in the method according to the present invention, the exhaust effluent is extracted from the preheating shaft and is at least partially introduced in the calcining shaft with a comburant. This can be done either by a separated injection of a comburant and the exhaust effluent or by injection of a comburant mixture containing the exhaust effluent and a comburant. The comburant is preferably a $O_2$-rich gas, such as dioxygen. Accordingly, the method according to the present invention carries out fuel combustion in a comburant and a recirculated gas which results in exhaust effluent containing the combustion fumes and $CO_2$ from decarbonation of the carbonate stones and results 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 from the preheating shaft. This evidently results in a significant increase in the $CO_2$ content of the exhaust effluent discharged from the top of the kiln, compared to the conventional method.

According to the invention, an exhaust 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 kiln to the greenhouse effect.

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

To keep the concentration in $CO_2$ high enough, the cooling gas entering the kiln, preferably from the bottom of the shaft or of the shafts, flows upwardly through the cooling zone in counter-current with the calcined stones descending in the shafts. The cooling gas is then heated by heat exchange with the calcined stones and is extracted outside of said kiln before it can mix with the effluent gas stream.

According to the present invention, the extraction of the heated cooling gas is performed as follows :

- the heated cooling gas is extracted from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode peripherally through a collector peripheral ring in fluid connection with the cooling zone, at a level located below the connecting channel and from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through a central collector element in fluid communication with said cooling zone and
- the heated cooling gas is extracted from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through a central collector element in fluid communication with said cooling zone and from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through a collector peripheral ring in fluid connection with the cooling zone, at a level located below the connecting channel.

It has been indeed identified according to the present invention that the heated cooling gas should be extracted at different

location depending to the role of the shaft and the period in the cycle of calcining/preheating to maximize the recovery of $CO_2$ and keep as low as possible cooling gas leakage.

In the calcining shaft, the combustion fumes and the $CO_2$ exhausted from the decarbonatation of the carbonate stone form the exhaust effluent and is concentrated around the central vertical axis of the cooling zone. Due to its momentum, the exhaust effluent pushes the heated cooling gas towards the walls of the cooling zone.

In the preheating shaft, the exhaust effluent arrives from the calcining shaft and is mainly spread towards the walls of the cooling zone. Due to its momentum, the exhaust effluent pushes the heated cooling gas to the central region of the cooling zone.

The collector peripheral ring is in fluid communication with the cooling zone of the kiln, for example with a annular space void of stone created by the descending stones below the connecting channel.

The process according to the present invention foresees an extraction step of the heated cooling gas in the calcining shaft in majority (from 50 to 100%) by volume on dry gas basis relative to the introduced cooling air in the same shaft peripherally through a collector peripheral ring in fluid connection with the cooling zone, at a level located below the connecting channel, i.e. in the portion of the calcining shaft where the heated cooling gas is mainly directed by the exhaust effluent, while a minority (from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft) portion of the heated cooling gas may be at the same time extracted from a central collector element in fluid communication with the cooling zone of the calcining shaft.

The process according to the present invention also foresees an extraction step of the heated cooling gas in the shaft in preheating mode, in majority (from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft) through a central collector

element in fluid communication with said cooling zone since in that shaft, the exhaust effluent, with the higher momentum, pushes the heated cooling gas to the central region of the cooling zone and in minority (from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft) through a collector peripheral ring in fluid connection with the cooling zone, at a level located below the connecting channel.

Thereby, the fact that in the calcining shaft the cooling gas is extracted in majority in periphery, below the connecting channel and that in the preheating shaft is extracted in majority to a central collector allow to minimize the $CO_2$ dilution of the exhaust effluent by minimizing leakage of cooling gas in the exhaust effluent, but also reduce the leakage of $CO_2$ in the cooling gas where it ends ultimately lost.

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 ($kg*m/s^2$).

Advantageously, the heated cooling gas is extracted from 70 to 100%, preferably from 75 to 99%, more preferably from 80 to 98% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode in periphery through said collector peripheral ring and from 0 to 30%, preferably from 1 to 25%, more preferably from 2 to 20% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through said central collector element and the heated cooling gas is extracted from 0 to 30%, preferably from 1 to 25%, more preferably from 2 to 20% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through said collector peripheral ring and from 70 to 100%, preferably from 75 to 99%, more preferably from 80 to 98% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through said central collector element.

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 calcining mode. Preferably, the loading of carbonate mineral stones occurs at the top of the shaft that works in a preheating mode.

In a preferred embodiment of the present invention, the process further comprises a CO reduction step in the connecting channel by injecting a mixing gas 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.

The momentum ratio between a mixing gas and the combustion fumes flow is defined as the ratio of the momentum of the mixing gas and the momentum of the combustion fumes. The momentum of the mixing gas 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 through entry means at high velocity in the connecting channel. The mixing gas can be steam, $O_2$-rich stream or $CO_2$-rich stream such as the exhaust effluent.

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 and the exhaust effluent.

It must be noted that the mixing gas does not require to be continuous or constant. It can be advantageous to enhance mixing to supply the mixing gas 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.

Advantageously, the exhaust effluent is partially or fully collected in at least one buffer after said exhausting step.

Preferably, said 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.

In one advantageous embodiment, said cooling step comprises a supply of cooling gas at the bottom of each of said shafts with the same rate of supply or a different rate of supply between the calcining shaft and the preheating shaft.

In yet an advantageous embodiment, in the process according to the present invention, said 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.

In another advantageous embodiment, 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 a particular embodiment, said exhaust effluent, exhausted from the top of said at least one shaft in preheating mode injected, at least partially to the shaft in calcining mode is injected directly or indirectly:

- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode, or
- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode and to the preheating shaft, for example in the preheating zone, or
- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode and in the connecting channel, for example in the cross-over channel, or
-
- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode, in the connecting channel, for example in the cross-over channel and to the preheating shaft, for example in the preheating zone or at the outlet of the fuel lances.

Within the meaning of the present invention, the wording "injected indirectly" means that the injection can be done from a temporary device, such as for example from a buffer or a storage reservoir, located between the origin of the exhaust effluent and the injection point(s).

In yet a preferred embodiment the present invention further comprises at least one heat exchange between the heated cooling gas, which has been extracted outside the kiln, and said recirculated fraction of exhaust effluent, for example before injection at least partially to the shaft in calcining mode.

In yet a preferred embodiment the present invention further comprises at least one heat exchange between the heated cooling gas, which has been extracted outside the kiln, and said recirculated fraction of exhaust effluent for example before injection

- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode, or
- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode and to the preheating shaft, for example in the preheating zone, or
- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode and in the connecting channel, for example in the cross-over channel, or
- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode, in the connecting channel, for example in the cross-over channel and to the preheating shaft, for example in the preheating zone or at the outlet of the fuel lances.

In a particular embodiment of 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 exhaust effluent discharged from the kiln, or using another source of $CO_2$ as a carrier gas.

In another particular embodiment, a portion of the exhaust effluent discharged from the kiln is introduced in lances for fuel injection or in an outer envelope, enclosing lances for fuel injection for cooling said lances.

The outer envelope is typically a sleeve inside which the lance is concentrically installed having a proximal end and a distal end. The outer envelope can have one proximal inlet and one proximal outlet both installed in proximity of the proximal end, for respectively feeding and exiting the exhaust effluent inside the outer envelope. In a variant, the out envelope is a through-sleeve, where the proximal end is an open end for admitting the exhaust effluent and the distal end is an open end for abutting in the combustion zone and exiting the exhaust effluent around the lance or the injected fuel. The exhaust effluent can further sleeve the fuel in a portion close to the end of the outer envelope.

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 amount of oxygen introduced in the kiln available for combustion 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 gas temperature in the combustion zone is comprised between 900°C and 1500 °C, more preferably between 1000°C and 1400°C or between 1100°C and 1300°C.

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.

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).

In a further advantageous embodiment of the present invention, the process 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 particular embodiment of the present invention, said mixing gas is exhaust effluent or substantially pure $CO_2$ gas, optionally fed from the storage unit and/or the buffer, $O_2$-rich gas or steam.

In a further preferred embodiment, 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.

Preferably, by the terms $O_2$-rich gas or stream, it is meant according to the present invention, a gas 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 gas 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.

In a particularly preferred embodiment, during the step of recirculating said fraction of the exhaust effluent and before the step of injecting the exhaust effluent to the kiln, the exhaust effluent is cooled into a heat exchanger in which at least a part of the water vapour is condensed and discarded forming a cooled and dried exhaust effluent.

Within the meaning of the present invention, by the wording "dried exhaust effluent", it is meant a gaseous effluent substantially

depleted in water vapor. Obviously, in the dried exhaust effluent, some % of water vapor can remain.

Preferably, according to the present invention, a portion of the cooled and dried exhaust effluent is further introduced to the kiln, such as for example at the top of the shaft in calcining mode at a temperature below 350°C, preferably below 200°C, preferably below 100°C, more preferably between 30 and 50°C.

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

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

The present invention also relates to a parallel-flow regenerative kiln for implementing the method according to anyone of the preceding claims, 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, an exhaust effluent discharge duct at the top of the shafts, which is connected to a chimney, and
- a supply of cooling gas to cool the calcined material produced,

the kiln 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 exhaust effluent discharge duct of the shafts and said oxidant supply openings of the shafts,
- a separating member, capable of collecting a portion of exhaust effluent discharged from the kiln via the duct and introducing it into the recirculation circuit, and
- a source of concentrated dioxygen, 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,

wherein the shafts have a circular cross-section and said connecting channel is a connecting channel that connects the peripheral channels arranged around each shaft so as to allow a transfer of gas,

said kiln being characterized in that below the connecting channel, the shafts are provided, , with a collector peripheral ring connected with a first extracting element so as to allow heated cooling gas to be removed from the kiln, said first extracting element being controlled by a first control means, and at the bottom with a central collector element connected with a second extracting element so as to allow heated cooling gas to be removed from the kiln, said second extracting element being controlled by a second control means, said first control means and said second control means being synchronized with said reversing system.

In a preferred embodiment, in the kiln according to the present invention, the first and the second extracting element both include at least one control element, able to extract, based on a signal respectively from the first or second control means, from 0 to 100% of the heated cooling gas.

In a further preferred embodiment, said connecting channel comprises a series of mixing gas entry means, provided to feed a mixing gas 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 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.

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 and the exhaust effluent.

In yet a further preferred embodiment, said connecting channel comprises a series of obstacles arranged to increase the mixing between said mixing gas and said combustion fumes.

Advantageously, according to the present invention, the parallel-flow regenerative kiln comprises, downstream or upstream the pressurization means, heating means to heat said mixing gas before injection in the connecting channel, said heating means being preferably chosen amongst a heat exchanger, a combustion chamber, electrical heater.

In a particular embodiment according to the present invention, the kiln comprises, as a dioxygen source for the recirculation circuit, a unit for separating air into dioxygen and dinitrogen.

In a further particular embodiment of the present invention, a heat exchanger supplied with heated cooling gas removed from the kiln, is mounted on the recirculation circuit.

In yet a further particular embodiment, the kiln according to the present invention comprises equipment for unloading calcined material that is resistant to temperatures greater than 100° C, preferably greater than 200°C, more preferably greater than 300°C, such as equipment in refractory steel.

Preferably, in the parallel-flow regenerative kiln according to the present invention, said recirculation circuit is connected to at least one buffer unit.

More preferably, said recirculation circuit is connected to storage unit provided to store a $CO_2$-rich exhaust effluent, optionally before or after a buffer unit.

In yet a preferred embodiment according to the present invention, said central collector element has a tubular central collecting element with at its lower end, at least one extraction outlet and, at its upper end located at a level lower than the connecting channel, a harvesting opening oriented axially upwards, each shaft further comprising a protective element which, fixed in the shaft in a position independent of the tubular central collecting element, covers the upper

end of the latter by surrounding it up to a level lower than the harvesting opening.

Preferably, the protective element is arranged above and at a distance from the harvesting opening, flaring downwards conically to a cylindrical lower part which extends coaxially and at a distance from the upper end of the tubular central collecting element, leaving between the upper end of the collecting element and the protective element, a free passage for collecting heated cooling gas through the opening of the central tubular collecting element, said protective element being supported centrally in the shaft by several support spacers, such as 4, 6, 8 or 10 spacers.

Other embodiments of the parallel-flow regenerative kiln according to the present invention are mentioned in the appended claims

Other characteristics and advantages of the present invention will be derived from the non-limitative following description, and by referring to the drawings and the examples.

In the drawings, figure 1 schematically shows a conventional PFRK kiln of circular cross-section.

Figure 2 schematically shows one embodiment of the kiln with a circular cross-section according to the invention carrying out one embodiment of the process according to the present invention.

Figure 3 schematically shows a further embodiment of the kiln with a circular cross-section according to the invention carrying out one embodiment of the process according to the present invention.

Figure 4 schematically shows a further embodiment of the kiln with a circular cross-section according to the invention carrying out one embodiment of the process according to the present invention.

Figure 5 schematically shows a further embodiment of the kiln with a circular cross-section according to the invention carrying out one embodiment of the process according to the present invention.

Figure 6 represents a numeric modelling of the oxygen concentration in weight% of the several flows in the PFRK according to the present invention.

Figure 7 schematically shows a variant of the embodiment of figure 3.

Figure 8 schematically shows a variant of the embodiment of figure 4.

In the drawings, the same reference numbers have been allocated to the same or analog element.

Conventionally, the shaft shown on the left is in calcining 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 figure 1, the parallel-flow regenerative kiln shown is a vertical double-shaft kiln 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 calcining 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, progressively descend 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 exhaust gas 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 gas 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 gas 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 do not receive any fuel, but still can be supplied with cooling gas. The inlet 5 of the shaft in preheating mode is supplied by the carbonate stones. The opening 6 for supplying combustion air is closed. However, the supply duct 7 for the cooling gas 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 gas 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 kiln via a discharge duct 14 and transferred to a chimney 15, possibly after treatment in equipment such as filters. In the shaft in calcining mode 1, this discharge duct 14 is closed.

The kiln 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 kiln in such a way

that, in production mode, each shaft operates alternately in calcining mode and in preheating mode.

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

Figure 2 is a view of preferred embodiment of the kiln according to the present invention where the combustion of fuel is performed in oxy-combustion conditions, i.e. in presence of $CO_2$ and oxygen. As can be seen, this embodiment comprises a separating member 17, capable of collecting a portion of exhaust effluent discharged from the kiln 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 exhaust effluent is advantageously treated in a treatment unit 19, where it may, for example, be filtered and/or dried for example in a condensation unit. An air separation unit 20 separates air supplied by the duct 21 into $N_2$ discharged via the duct 22 and $O_2$ 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 exhaust effluent and concentrated $O_2$ to the top of each of the shafts at the supply opening 6.

While this embodiment is illustrated with a feed of a mixture between the exhaust effluent and the oxygen, another embodiment, included within the scope of the present patent application can have a double feed, one for the exhaust effluent and one for the oxygen, even if less preferable because the composition of the gaseous atmosphere in the calcination zone can lack uniformity in the latter embodiment.

Further, the mixture or the separated input of exhaust effluent and oxygen is illustrated at the top of the shaft, it is also conceivable within the scope of the present invention to have a feed directly in the calcination zone.

The separating member 17 is continuously in service during combustion, the same as the treatment unit 19 and the air separation unit 20. Alternatively, when the air separation unit if followed by an oxygen storage unit, the air separation unit can run continuously in service or not.

As has already been seen, the reversing system 16 closes the discharge duct 14 at the top of the shaft in calcining 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, according to the present invention, the heated cooling gas is extracted outside the kiln after contact with the calcined material. A removal system is present in each shaft.

In more details, the shafts are provided, below the connecting channel, with a collector peripheral ring 25 connected with a first extracting element 26 so as to allow heated cooling gas to be removed from the kiln, said first extracting element 26 being controlled by a first control means (not shown), and at the bottom with a central collector element 27 connected with a second extracting element 28 so as to allow heated cooling gas to be removed from the kiln, said second extracting element 28 being controlled by a second control means (not shown), said first control means and said second control means being synchronized with said reversing system.

In the illustrated embodiment, the first extracting element 26 and the second extracting element 28 both include at least one control element, able to extract, based on a signal respectively from the first or second control means, from 0 to 100% of the heated cooling gas.

The control element of the first extracting element 26 connected to the collecting ring 25 of the shaft in calcining mode allows for example to extract from 50 to 100%, preferably from 70 to 100%, preferably from 75 to 99%, more preferably from 80 to 98% by volume on

dry gas basis relative to the introduced cooling air in the same shaft of heated cooling gas from the shaft in calcining mode through said collector peripheral ring 25, based on a signal from the first control means.

The control element of the second extracting element 28 connected to the central collector element 27 of the shaft in calcining mode allows to extract from 0 to 50%, preferably from 0 to 30%, preferably from 1 to 25%, more preferably from 2 to 20% by volume on dry gas basis relative to the introduced cooling air in the same shaft of heated cooling gas from the shaft in calcining mode through said central collector element, based on a signal from the second control means.

The control element of the first extracting element 26 connected to the collecting ring 25 of the shaft in preheating mode allows for example to extract from 0 to 50%, preferably from 0 to 30%, preferably from 1 to 25%, more preferably from 2 to 20% by volume on dry gas basis relative to the introduced cooling air in the same shaft of heated cooling gas from the shaft in preheating mode through said collector peripheral ring 25, based on a signal from the first control means.

The control element of the second extracting element 28 connected to the central collector element 27 of the shaft in preheating mode allows to extract from 50 to 100%, preferably from 70 to 100%, preferably from 75 to 99%, more preferably from 80 to 98% by volume on dry gas basis relative to the introduced cooling air in the same shaft of heated cooling gas from the shaft in preheating mode through the central collector element 27, based on a signal from the second control means.

Moreover, in order to recover a portion of the energy from the hot air removed by the extraction element 26, (but also possibly 28) a heat exchange may be provided with the portion of recirculated exhaust 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 exhaust effluent discharged from the kiln using an injection duct 37 may also be provided, preferably at a high velocity to create turbulence and reduce the CO concentration in the exhaust effluent, during the passage of said combustion fumes towards the at least one shaft working in a preheating mode. The ratio of momentum J between the collected portion of exhaust effluent and the combustion fumes is preferably higher than 1.

Optionally beforehand, a heat exchange between the heated cooling gas removed from the kiln, and this above-mentioned fraction to be injected may occur using a heat exchanger, for example the heat exchanger 36. In the absence or in complement thereof, another heater not shown may be provided on the injection duct 37.

Optionally, the extracted heated cooling air can be provided to a treatment unit (not represented) or to a heat exchanger for heat recovery, such a in a drying unit or to a power generation unit.

Preferably, in the connecting channel or crossover channel 3, the injection of a fraction of said collected portion of exhaust effluent discharged from the kiln 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.

Figure 3 illustrates a variant of figure 2, where the extracting element have a closed position and an open position.

In this embodiment, the first extracting element connected to the collecting ring 25 of the shaft in calcining mode is in open position to extract nearly 100% by volume of heated cooling gas on dry gas basis relative to the introduced cooling air in the same shaft and the second extracting element connected to the central collector element 27 of the shaft in calcining mode is in closed position to not extract cooling gas or

only extract a very few % of the heated cooling gas due to some unavoidable leakage.

The first extracting element connected to the collecting ring 25 of the shaft in preheating mode is in closed position to not extract cooling gas or almost extract a very few % of the heated cooling gas due to some unavoidable leakage and the second extracting element connected to the central collector element 27 of the shaft in preheating mode is in open position to extract nearly 100% of heated cooling gas by volume on dry gas basis relative to the introduced cooling air in the same shaft.

Figure 4 illustrates another advantageous embodiment of the kiln according to the present invention. As can be seen, this embodiment is similar to the embodiment of the kiln described in Figure 3 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 to reduce the CO content of the exhaust effluent.

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 (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.

Figure 5 is a view of another advantageous kiln according to the present invention. As can be seen, this embodiment is similar to the embodiment of the kiln described in figure 4 with a special design of the central collector element.

At the bottom of each shaft, a central collector element 27 is located having a tubular central collecting element 29 with at its lower end, at least one extraction outlet 30 and, at its upper end located at a level lower than the connecting channel 3, a harvesting opening 31 oriented axially upwards. Through this opening 31, the cooling gas heated in contact with the decarbonated calcined material is collected inside the central tubular collecting element 29, so as to allow its extraction from the kiln. In the example illustrated, this heated colling gas extracted from the kiln is transferred, using a draft fan 32, to a heat exchanger 36 mounted on the recirculation circuit 18, so as to preheat the part taken from the exhaust effluent leaving the oven, preferably before mixing with concentrated oxygen.

Each shaft further comprises a protective element in the form of a cap 33 which, fixed in the shaft in a position independent of the tubular central collecting element 29, covers the upper end of the latter by surrounding it up to a level lower than the harvesting opening 31. In the illustrated example an upper part of the protective element in the form of a hat 33 is arranged above and at a distance from the harvesting opening 31, flaring downwards conically to a cylindrical lower part which extends coaxially and at a distance from the upper end of the tubular central collecting element 29. This arrangement thus leaves, between the upper

end of the collecting element 29 and the cap 33, a free passage for collecting heated cooling gas through the opening 30 of the central tubular collecting element. The protective element in the form of a hat 33 is supported centrally in the shaft by several support spacers 34, here 4 spacers. The several elements of the central collecting element 34 can be also cooled with circulating fluid, as for example described in patent application EP 23190297.4.

Figure 6 represents a numerical modeling of the Parallel-flow regenerative kiln with a circular section showing the path of the gases as a function of their oxygen content. It only shows the combustion zone B, from the end of the lances, and the cooling zone C, and therefore the top of the shafts is not represented.

Zones a: in the shaft in calcining mode, combustion oxygen mixed with exhaust fumes, content of oxygen can be about 20-25% or even a bit more when working in oxygen excess in the combustion zone.

Zones b: jets of combustion fumes emitted by the lances, in which there is almost no more oxygen and between which we can still find a little O2 which has not reacted.

Zone c: the fumes penetrate deep into cooling zone C, mixing little by little with the cooling gas, such as cooling air. They push the gas mixture peripherally into the peripheral channel and then into the cross-over channel 3.

Zone d: in the shaft in preheating mode, cooling gas/air.

Zone e: mixture between the gas stream coming from the peripheral channel and the cooling gas/air. The more we progress towards the center of the shaft, the more the residual O2 content increases.

Zone f : exhaust effluent in the shaft in preheating mode,

Zone g: exhaust effluent in the shaft in calcining mode and heated cooling gas/air in the shaft in preheating mode.

Figure 7 illustrates another advantageous embodiment of the kiln according to the present invention. As can be seen, this embodiment is similar to the embodiment of the kiln described in Figure 3 but where the heat exchanger 36 is positioned in the injection duct 37.

Figure 8 illustrates another advantageous embodiment of the kiln according to the present invention. As can be seen, this embodiment is similar to the embodiment of the kiln described in Figure 4 but where the heat exchanger 36 in a derivation of the recirculation circuit to preheat exhaust effluent before the entry into a combustion chamber 44 fed by oxygen-rich gas stream 41, fuel 45 and the exhaust effluent.

**Examples.-**

**Comparative example 1.-**

A parallel flow regenerative kiln according to the present invention having a capacity of 300 TPD of calcined mineral stones, where fuel is burned in oxy-fuel conditions has been numerically modelized. The kiln comprises a central collecting element and a peripheral circular collecting channel.

The kiln has a specific heat consumption of 4.1 GJ/ton of mineral stones. Cooling air is introduced at a specific flow rate of 0.9 $Nm^3/kg$ of mineral stones and the temperature of the gas entering the burning zone is 600°C. The temperature in the cross-over channel is 1251°C, calculated as an average gas temperature in the connecting channel mid-way between the shafts. The calcined mineral stones has a calcination weight% of 98.8 (meaning than 1.2 weight % of the mineral stones is still under its carbonated form.

The cooling air was only extracted through the peripheral circular collecting channel in the calcining shaft and in the preheating shaft. The peripheral circular collecting channel comprises 8 extraction port with 1 having a smaller size due to the presence of a pillar.

**Table 1.- $CO_2$ capture performance**

| | |
|---|---|
| $CO_2$ leakage in calcining shaft (Kg/h) | 440 |
| $CO_2$ leakage in preheating shaft (Kg/h) | 690 |
| Total $CO_2$ leakage in cooling zone (Kg/h) | 1130 |
| Total kiln $CO_2$ Input (Kg/h) | 10089 |
| $CO_2$ capture efficiency (% vol on dry basis) | 88.8 |

**Table 2.- Cooling air capture performance**

| | |
|---|---|
| $N_2$ leakage in calcining shaft (Kg/h) | 400 |
| $N_2$ leakage in preheating shaft (Kg/h) | 600 |
| Total $N_2$ leakage in cooling zone (Kg/h) | 1000 |
| Total cooling air $N_2$ Input (Kg/h) | 11140 |
| Cooling air capture efficiency (% vol on dry basis) | 91.02 |

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**Comparative example 2.-**

The same parallel flow regenerative kiln according to comparative example 1 was numerically modelized.

The kiln has a specific heat consumption of 3.9 GJ/ton of mineral stones. Cooling air is introduced at a specific flow rate of 0.9 $Nm^3/kg$ of mineral stones and the temperature of the gas entering the burning zone is 700°C. The temperature in the cross-over channel is 1296°C, calculated as an average gas temperature in the connecting channel mid-way between the shafts. The calcined mineral stones has a calcination weight% of 100 (meaning than 1.2 weight % of the mineral stones is still under its carbonated form.

The cooling air was only extracted through the central collector element from the calcining shaft and the preheating shaft.

**Table 3.- $CO_2$ capture performance**

| | |
|---|---|
| $CO_2$ leakage in calcining shaft (Kg/h) | 530 |
| $CO_2$ leakage in preheating shaft (Kg/h) | 150 |
| Total $CO_2$ leakage in cooling zone (Kg/h) | 680 |
| Total kiln $CO_2$ Input (Kg/h) | 10303 |
| $CO_2$ capture efficiency (% vol on dry basis) | 93.4 |

**Table 4.- Cooling air capture performance**

| | |
|---|---|
| $N_2$ leakage in calcining shaft (Kg/h) | 470 |
| $N_2$ leakage in preheating shaft (Kg/h) | 130 |
| Total $N_2$ leakage in cooling zone (Kg/h) | 600 |
| Total cooling air $N_2$ Input (Kg/h) | 11140 |
| Cooling air capture efficiency (% vol on dry basis) | 94.61% |

**Example 1.-**

The same parallel flow regenerative kiln according to comparative example 1 was numerically modelized.

The kiln has a specific heat consumption of 3.9 GJ/ton of mineral stones. Cooling air is introduced at a specific flow rate of 0.9 $Nm^3/kg$ of mineral stones and the temperature of the gas entering the burning zone is 700°C. The temperature in the cross-over channel is 1296°C, calculated as an average gas temperature in the connecting channel mid-way between the shafts. The calcined mineral stones has a calcination weight% of 100 (meaning than 1.2 weight % of the mineral stones is still under its carbonated form.

The cooling air was extracted through the central collector element from the preheating shaft and from the peripheral circular collector peripheral ring from the calcining shaft.

**Table 5.- $CO_2$ capture performance**

| | |
|---|---|
| $CO_2$ leakage in calcining shaft (Kg/h) | 440 |
| $CO_2$ leakage in preheating shaft (Kg/h) | 150 |
| Total $CO_2$ leakage in cooling zone (Kg/h) | 590 |
| Total kiln $CO_2$ Input (Kg/h) | 10303 |
| $CO_2$ capture efficiency (% vol on dry basis) | 94.18 |

**Table 6.- Cooling air capture performance**

| | |
|---|---|
| $N_2$ leakage in calcining shaft (Kg/h) | 400 |
| $N_2$ leakage in preheating shaft (Kg/h) | 130 |
| Total $N_2$ leakage in cooling zone (Kg/h) | 530 |
| Total cooling air $N_2$ Input (Kg/h) | 11140 |
| Cooling air capture efficiency (% vol on dry basis) | 95.24 |

It should be understood that the present invention is not limited to the described embodiments and that variations can be applied without going outside of 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 (3, 13), comprising, in standard operation,

- loading carbonate mineral stones at the top of each shaft (1, 2),
- preheating these loaded stones in a preheating zone,
- calcining these preheated stones in a calcination zone with production of a decarbonated calcined material (10),
- cooling the calcined material (10) with cooling gas in a cooling zone, with formation of heated cooling gas by heat exchange,
- discharging the calcined material (10) from the bottom of the shafts (1, 2),
- exhausting an exhaust effluent from the kiln,
- each shaft alternately working in a calcining mode and in a preheating mode, one shaft working in a calcining 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 (11) descending co-currently in the shaft in calcining mode, and
  - through said connecting channel (3, 13), a passage of said combustion fumes (11) 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 combustion fumes coming from the connecting channel (3, 13), which is ascending and flows in counter-current through the loaded carbonate mineral stones, and
  - said exhausting step of said combustion fumes (11) as exhaust effluent at the top of said at least one shaft in preheating mode,

said method further comprises

- recirculating a fraction of the exhaust effluent exhausted from the top of said at least one shaft in preheating mode,
- injecting the exhaust effluent, exhausted from the top of said at least one shaft in preheating mode, at least partially 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, said comburant being preferably $O_2$-rich gas
- extracting said heated cooling gas outside of said kiln,

characterized in that during said extracting step of the heated cooling gas outside of the kiln, the heated cooling gas is extracted from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through a collector peripheral ring (25) in fluid connection with the cooling zone, at a level located below the connecting channel (3), and from 0 to 50% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through a central collector element (27) in fluid communication with said cooling zone and the heated cooling gas is extracted from 0 to 50% by volume on dry gas basis relative to the

introduced cooling air in the same shaft from the shaft in preheating mode through a collector peripheral ring (25) in fluid connection with the cooling zone, at a level located below the connecting channel (3) and from 50 to 100% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through a central collector element (27) in fluid communication with said cooling zone.

2. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to claim 1, wherein the heated cooling gas is extracted from 70 to 100%, preferably from 75 to 99%, more preferably from 80 to 98% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through said collector peripheral ring (25) and from 0 to 30%, preferably from 1 to 25%, more preferably from 2 to 20% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in calcining mode through said central collector element (27) and the heated cooling gas is extracted from 0 to 30%, preferably from 1 to 25%, more preferably from 2 to 20% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through said collector peripheral ring (25) and from 70 to 100%, preferably from 75 to 99%, more preferably from 80 to 98% by volume on dry gas basis relative to the introduced cooling air in the same shaft from the shaft in preheating mode through said central collector element (27).

3. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the claims 1 or 2, further comprising a CO reduction step in the connecting channel (3, 13) by injecting a mixing gas 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 (11) is higher than 1.

4. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the claims 1 to 3, wherein the

exhaust effluent is partially or fully collected in at least one buffer after said exhausting step.

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

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

7. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the claims 1 to 5, 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.

8. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln 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 and preferably air.

9. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the preceding claims wherein said exhaust effluent, exhausted from the top of said at least one shaft in preheating mode is injected, at least partially, to the shaft in calcining mode directly or indirectly:

- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode, or

- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode and to the preheating shaft, for example in the preheating zone, or

- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode and in the connecting channel, for example in the cross-over channel, or

- in the shaft in calcining mode in an upper portion of the shaft in calcining mode or in the combustion zone of the shaft in calcining mode, in the connecting channel (3, 13), for example in the cross-over channel (3) and to the preheating shaft, for example in the preheating zone or at the outlet of the fuel lances (4).

10. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln 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 exhaust effluent discharged from the kiln, or using another source of $CO_2$ as a carrier gas.

11. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the preceding claims, wherein a portion of the exhaust effluent discharged from the kiln is introduced in the lances (4) or in an outer envelope, enclosing lances (4) for fuel injection for cooling said lances (4).

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

13. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the preceding claims, wherein said mixing gas is exhaust effluent or substantially pure $CO_2$ gas, optionally fed from the storage unit and/or the buffer, $O_2$-rich stream or steam.

14. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln 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 (20), said separation unit (20) producing from an air entry, a stream of oxygen and a stream of nitrogen.

15. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the preceding claims, wherein during the step of recirculating said fraction of the exhaust effluent and before the step of injecting the exhaust effluent to the kiln the exhaust effluent is cooled into a heat exchanger (36) in which at least part of the water vapor is condensed and discarded forming a cooled and dried exhaust effluent.

16. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to claim 15, wherein a portion of the cooled and dried exhaust effluent is further introduced to the kiln, such as for example at the top of the shaft in calcining mode, at a temperature below 350°C, preferably below 200°C, preferably below 100°C, more preferably between 30 and 50°C.

17. 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,
- at least one supply opening (6) for oxygen-containing oxidant,
- an inlet (5), for loading carbonate mineral stones, at the top of the shafts (1, 2),
- an outlet (8) for unloading the calcined material produced, at the bottom of the shafts, an exhaust effluent discharge duct (14) at the top of the shafts (1, 2), which is connected to a chimney (15), and
- a supply of cooling gas (7) to cool the calcined material produced,

the kiln comprising a system (16) for reversing the operation of the shafts (1, 2), arranged so that each shaft (1, 2), 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 exhaust effluent discharge duct (14) of the shafts (1, 2) and said oxidant supply openings (6) of the shafts (1, 2),
- a separating member (17), capable of collecting a portion of exhaust effluent discharged from the kiln via the duct and introducing it into the recirculation circuit (18), and
- a source of concentrated dioxygen (20), 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 (11) from the shaft in calcining mode to at least one shaft in preheating mode,

wherein the shafts (1, 2) have a circular cross-section and said connecting channel (3, 13) comprises a cross-over channel (3) that connects the peripheral channels (13) arranged around each shaft (1, 2) so as to allow a transfer of gas,

said kiln being characterized in that below the connecting channel (3, 13), the shafts (1, 2) are provided with a collector peripheral ring (25) connected with a first extracting element (26) so as to allow heated cooling gas to be removed from the kiln, said first extracting element (26) being controlled by a first control means, and at the bottom with a central collector element (27) connected with a second extracting element (28) so as to allow heated cooling gas to be removed from the kiln, said second extracting element (28) being controlled by a second control means, said first control means and said second control means being synchronized with said reversing system (16).

18. Parallel-flow regenerative kiln according to claim 17, wherein the first (26) and the second extracting element (28) both include at least one control element, able to extract, based on a signal respectively from the first or second control means, from 0 to 100% of the heated cooling gas.

19. Parallel-flow regenerative kiln according to claim 17 or 18, wherein said connecting channel (3, 13) further comprises a series of mixing gas entry means, provided to feed a mixing gas from outside of the kiln into the lumen of the connecting channel (3, 13), said series of mixing gas entry means being operatively connected to a pressurization device so as to be able to inject a mixing gas at high velocity in said connecting channel (3, 13) 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.

20. Parallel-flow regenerative kiln according to any of the claims 17 to 19, wherein said connecting channel (3, 13) further comprises a series of obstacles arranged to increase the mixing between said mixing gas and said combustion fumes (11).

21. Parallel-flow regenerative kiln according to any of the claims 17 to 20, further comprising, downstream or upstream the pressurization means, heating means to heat said mixing gas before injection in the connecting channel, said heating means being preferably chosen amongst a heat exchanger (36), a combustion chamber, electrical heater.

22. Parallel-flow regenerative kiln according to any one of claims 17 to 21, wherein the kiln comprises, as a dioxygen source for the recirculation circuit (18), a unit (20) for separating air into dioxygen and dinitrogen.

23. Parallel-flow regenerative kiln according to any one of claims 17 to 22, wherein a heat exchanger (36) supplied with heated cooling gas removed from the kiln, is mounted on the recirculation circuit (18).

24. Parallel-flow regenerative kiln according to any one of claims 17 to 23, wherein it comprises equipment (24) for unloading calcined material that is resistant to temperatures greater than 100° C, preferably greater than 200°C, more preferably greater than 300°C, such as equipment in refractory steel.

25. Parallel-flow regenerative kiln according to any of the claims 17 to 24, wherein said recirculation circuit (18) is connected to at least one buffer unit.

26. Parallel-flow regenerative kiln according to any of the claims 17 to 25, wherein said recirculation circuit (18) is connected to

storage unit provided to store a $CO_2$-rich exhaust effluent, optionally before or after a buffer unit.

27. Parallel-flow regenerative kiln according to any of the claims 17 to 26, wherein said central collector element (27) has a tubular central collecting element (29) with at its lower end, at least one extraction outlet (30) and, at its upper end located at a level lower than the connecting channel 3, a harvesting opening (31) oriented axially upwards, each shaft (1, 2) further comprising a protective element (33) which, fixed in the shaft in a position independent of the tubular central collecting element (29), covers the upper end of the latter by surrounding it up to a level lower than the harvesting opening (31).

28. Parallel-flow regenerative kiln according to claim 27, wherein the protective element (33) is arranged above and at a distance from the harvesting opening (31), flaring downwards conically to a cylindrical lower part which extends coaxially and at a distance from the upper end of the tubular central collecting element (29), leaving between the upper end of the collecting element (29) and the protective element (33), a free passage for collecting heated cooling gas through the opening (30) of the central tubular collecting element (29), said protective element being supported centrally in the shaft by several support spacers (34), such as 4, 6, 8 or 10.

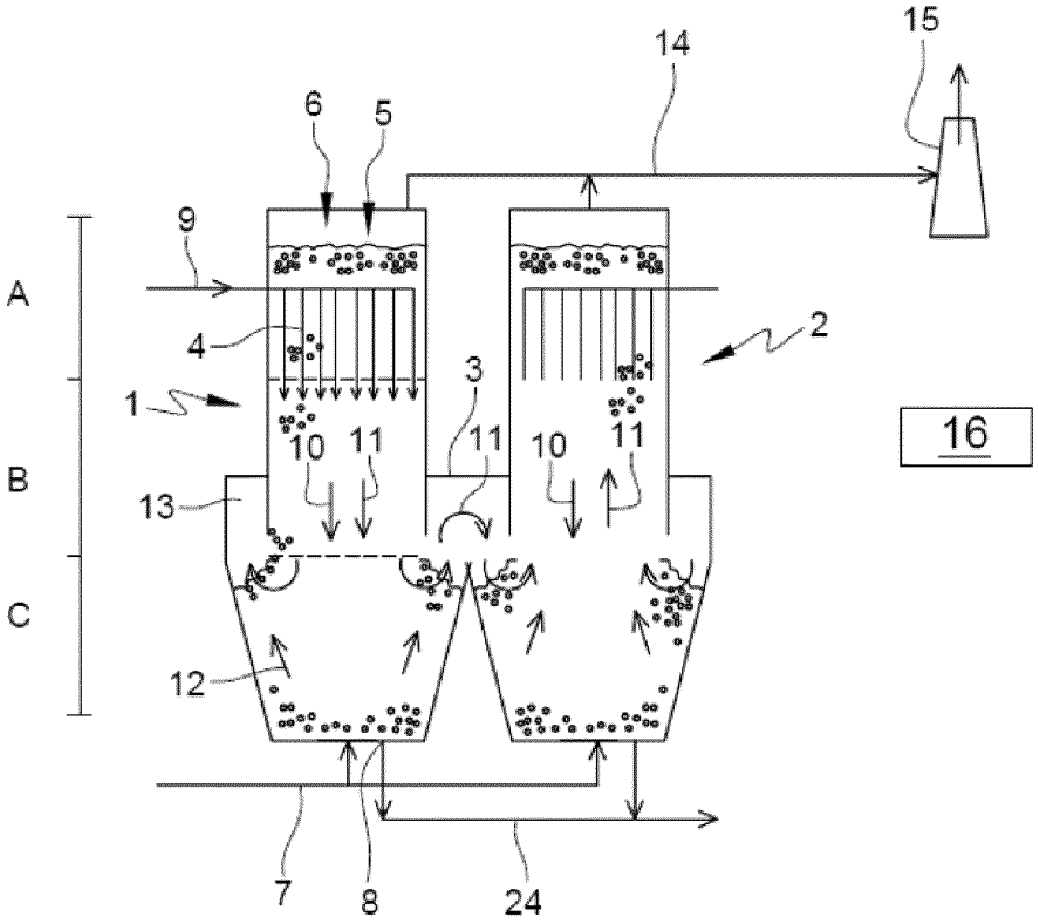



Fig 1

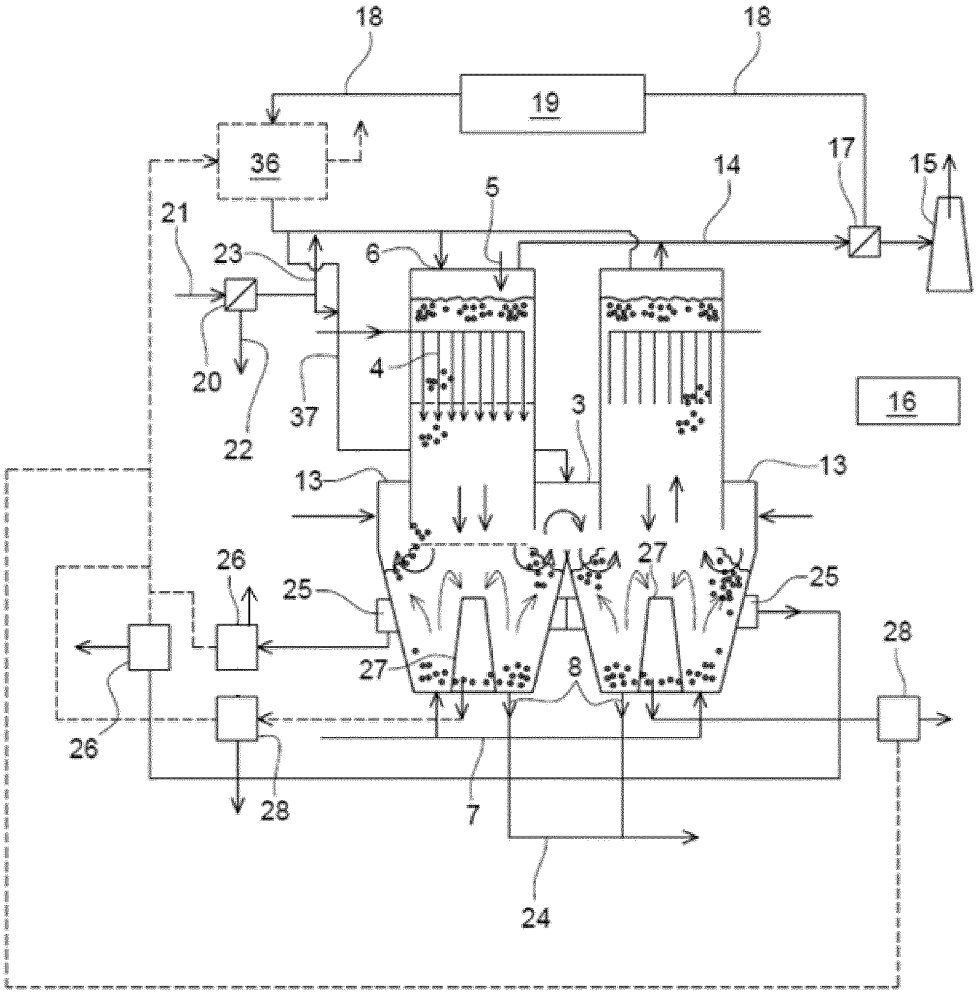

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Fig 2

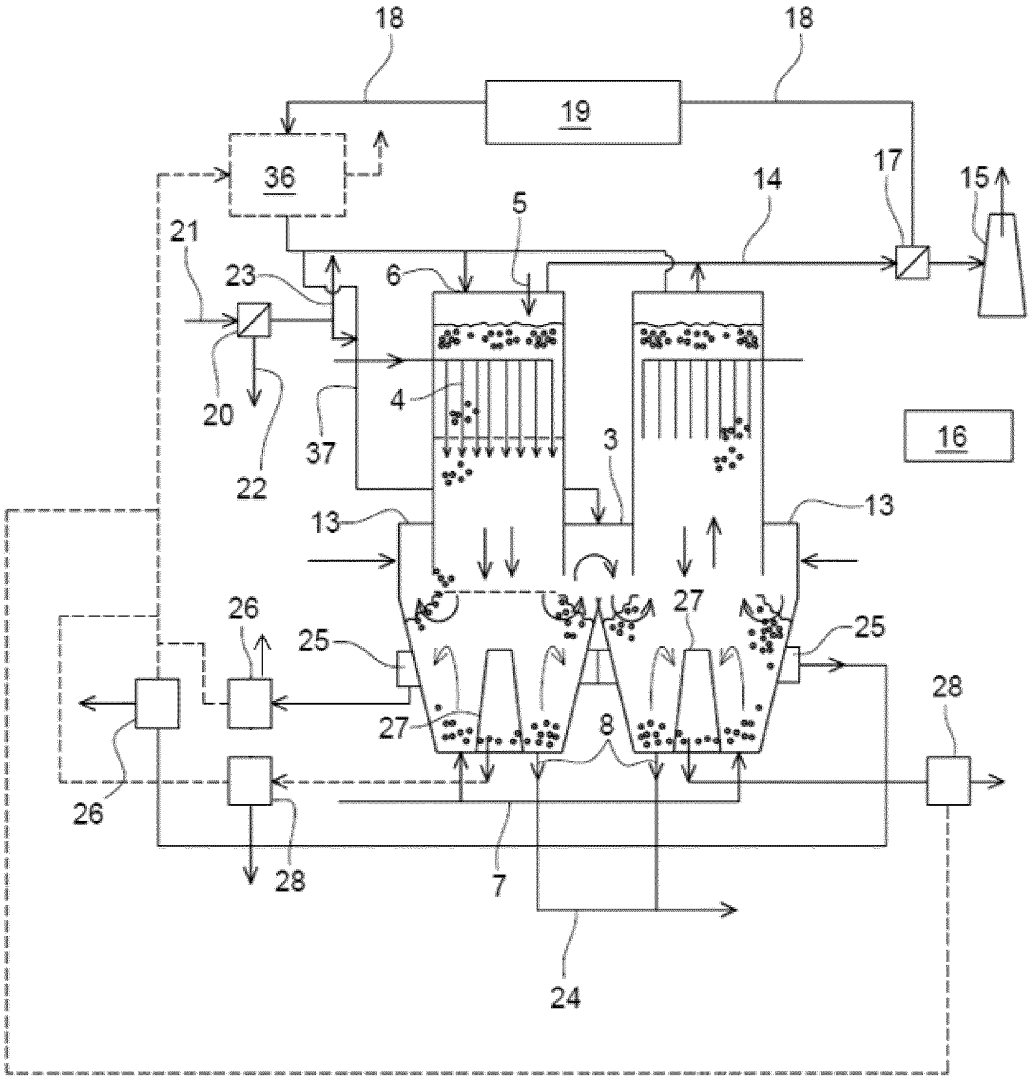

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Fig 3

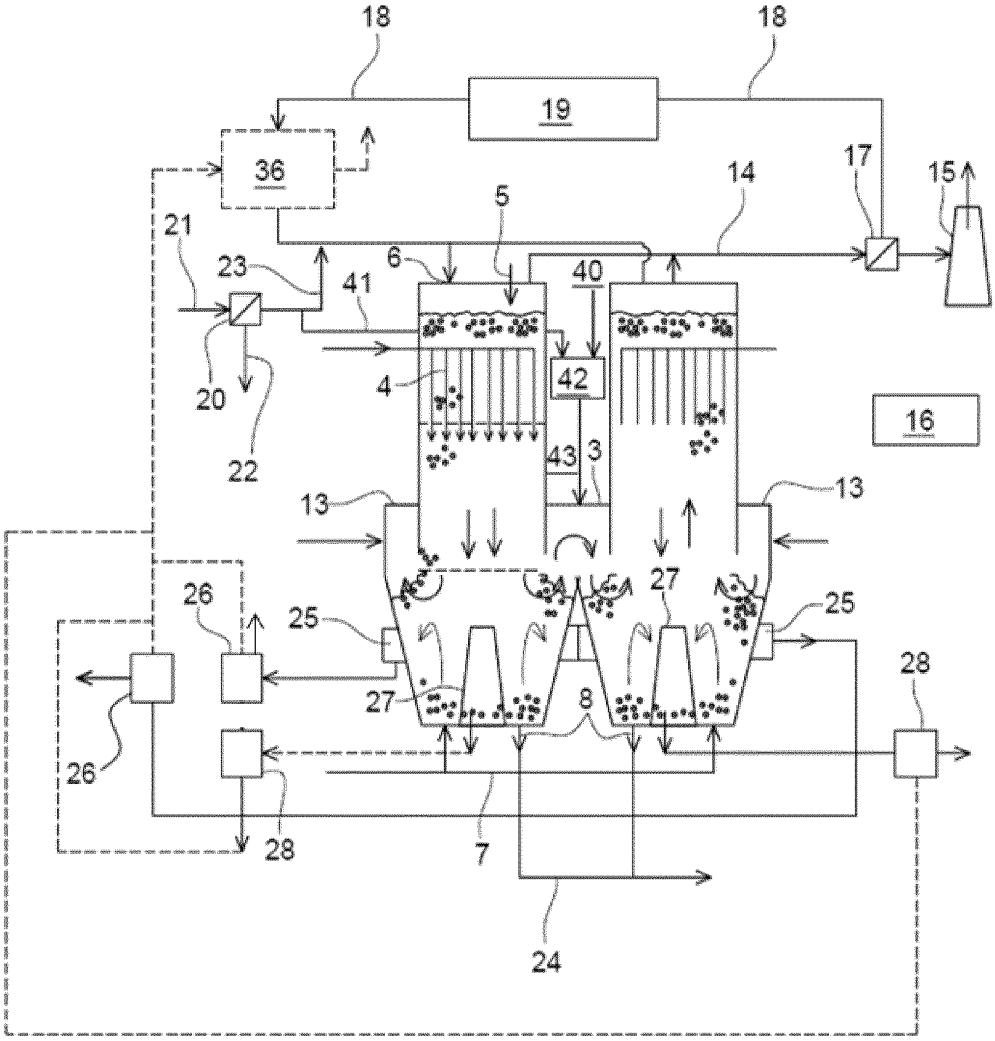

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Fig 4

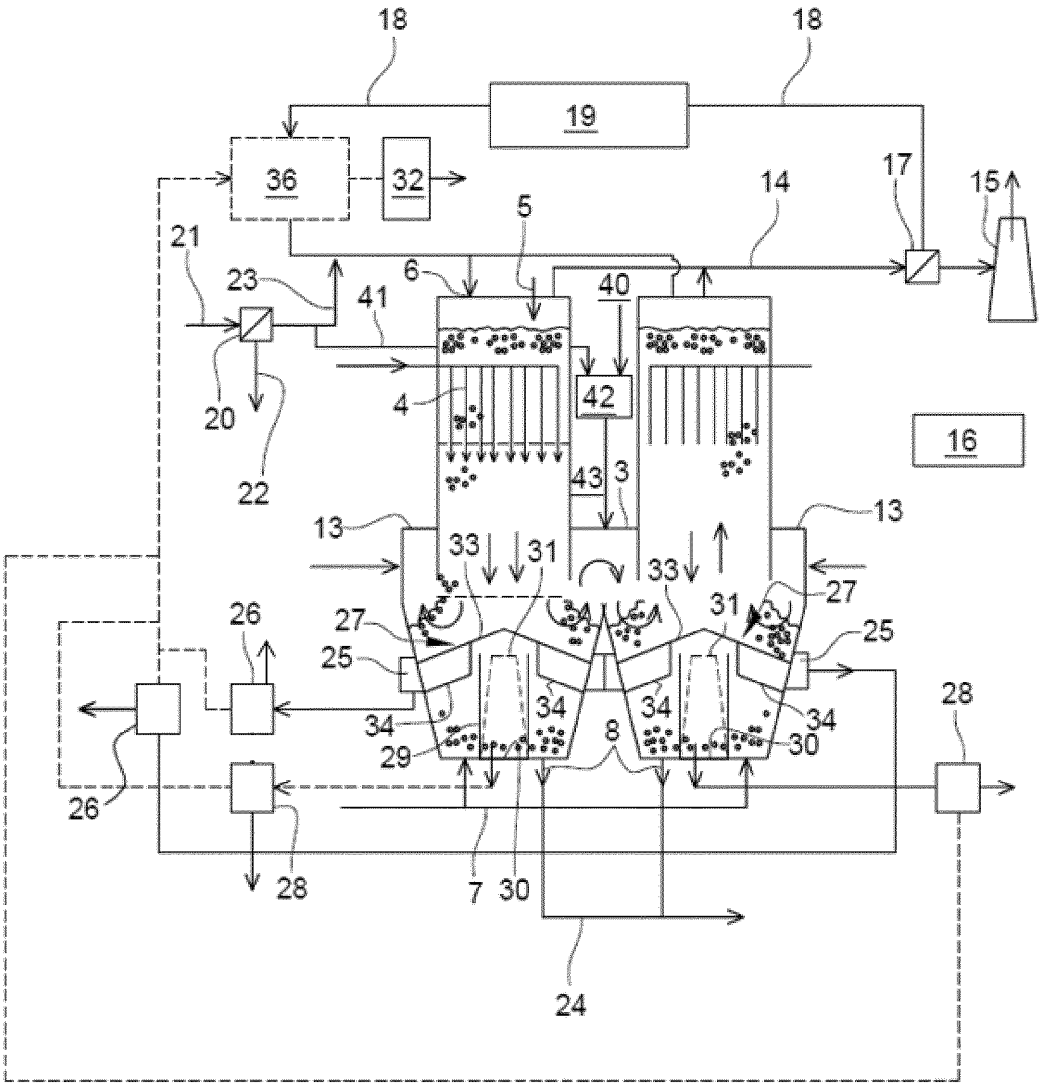

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Fig 5

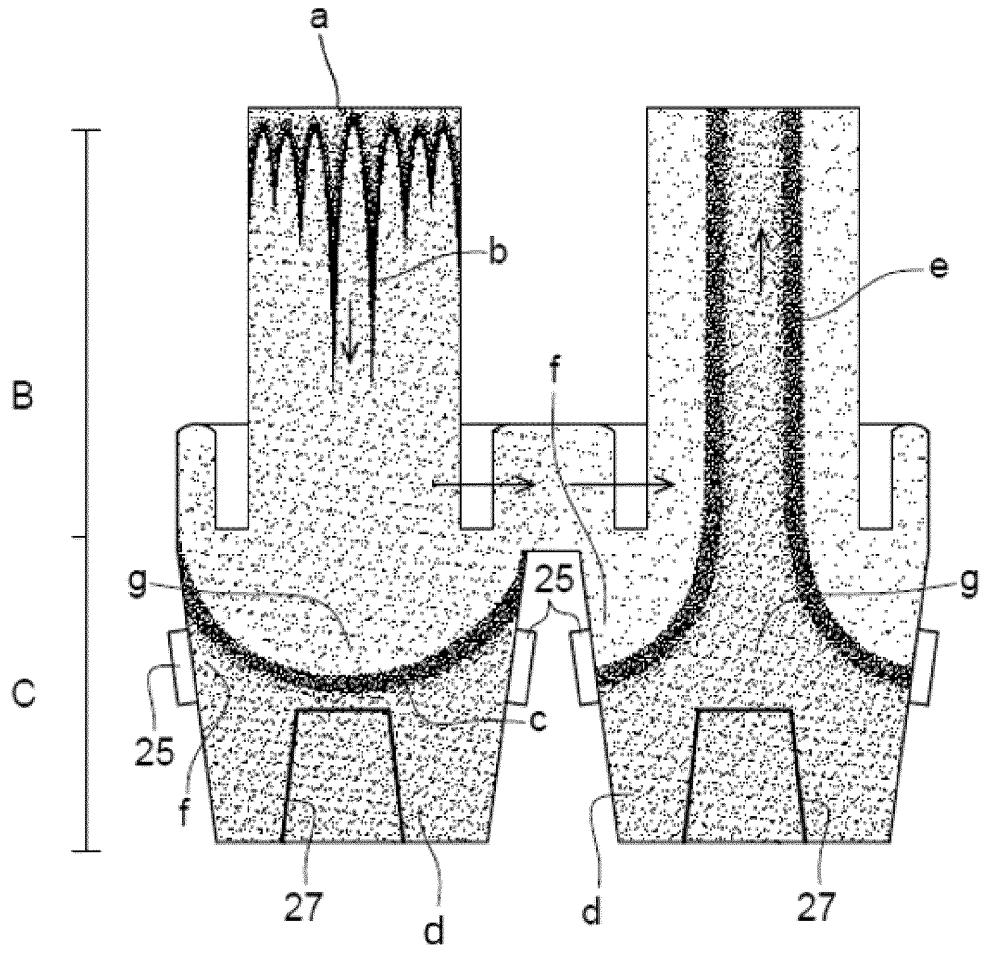



Fig 6

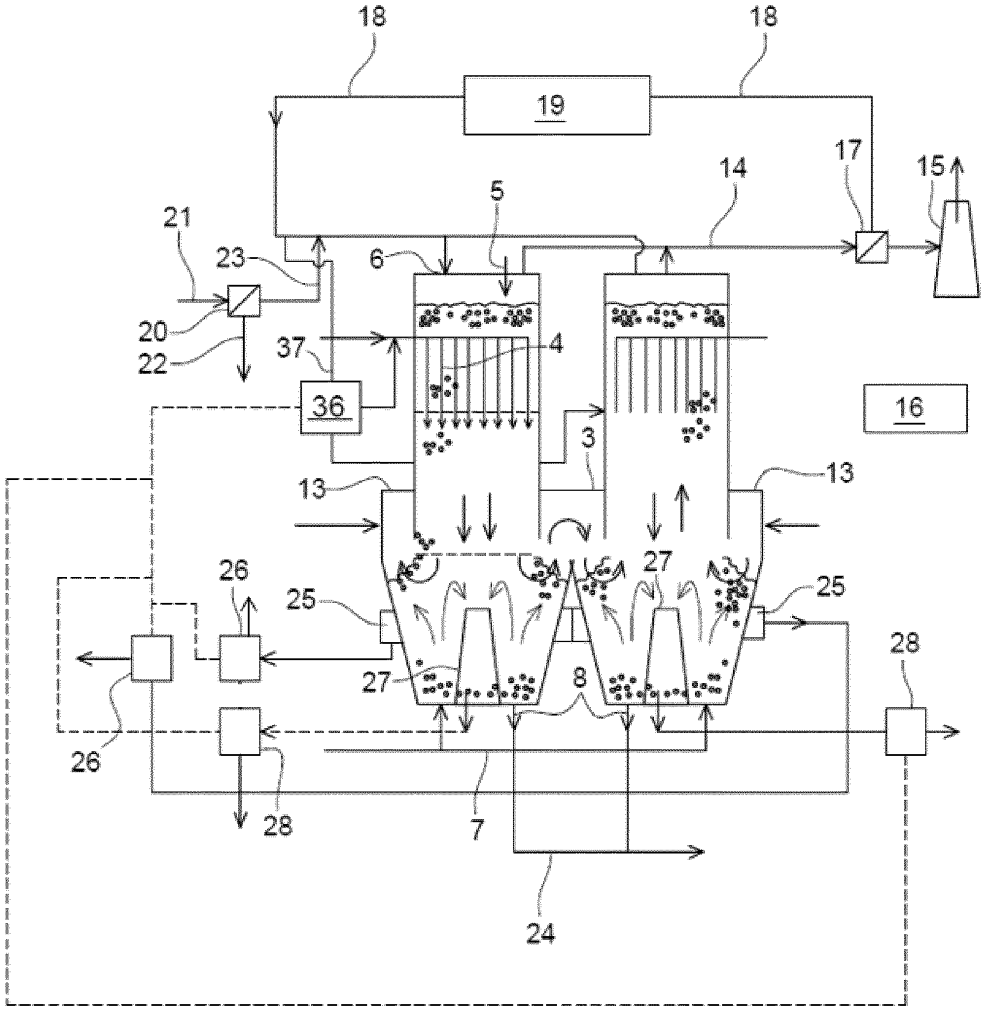

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Fig 7

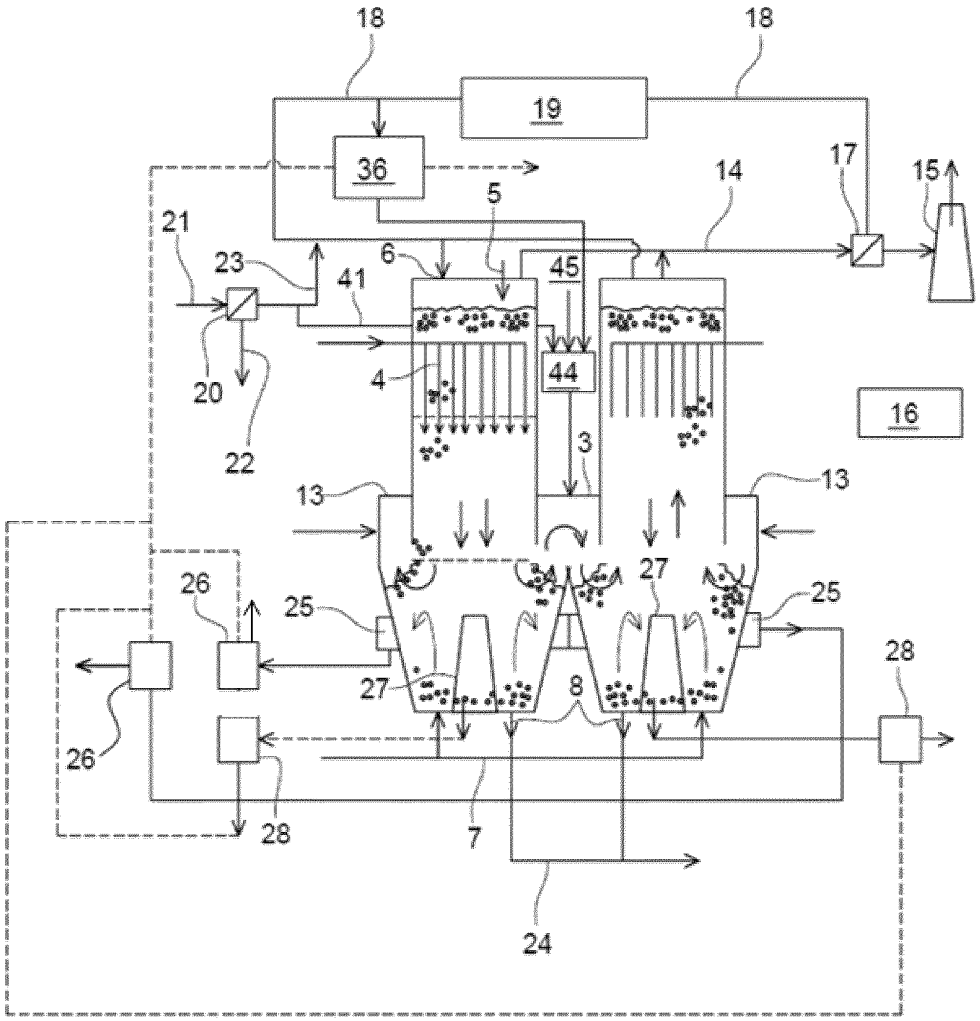

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Fig 8

# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/063970

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. F27B1/00 C04B2/12 F27B1/02 F27B1/22 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. |
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"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

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"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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 28 November 2024 | 17/12/2024 |

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

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# INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/063970

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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International application No
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