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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 November 2025 (27.11.2025)

WIPO | PCT

(10) International Publication Number
WO 2025/242288 A1

(51) International Patent Classification:
F27B 1/00 (2006.01) *F27B 1/22* (2006.01)
C04B 2/12 (2006.01) *F27B 1/26* (2006.01)
F27B 1/02 (2006.01)

(21) International Application Number:
PCT/EP2024/063973

(22) International Filing Date:
21 May 2024 (21.05.2024)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **S.A. LHOIST RECHERCHE ET DEVELOPPEMENT** [BE/BE]; Rue Charles Dubois 28, 1342 Ottignies Louvain-la-Neuve (BE).

(72) Inventors: **VAN CANTFORT, Olivier**; Avenue Gabriel Emile Lebon 169, 1150 Woluwe-Saint-Pierre (BE). **HABIB, Ziad**; Rue Arthur Van Dormael 10, 1630 Linkebeek (BE). **HALLAK, Bassem**; Schulstrasse 31, 39179 Barleben (DE).

(74) Agent: **CALYSTA NV**; Lambroekstraat 5A, 1831 Diegem (BE).

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

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

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

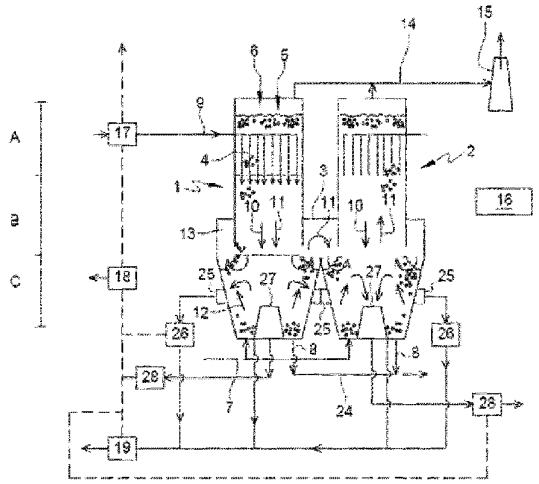


Fig. 4

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

[Continued on next page]

WO 2025/242288 A1

Published:

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

— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

« 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 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.

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.

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.

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 gas, by heat exchange,
- discharging the calcined material from the bottom of the shafts,
- exhausting a exhaust 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 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 gas 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 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 to increase 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 PFKR in oxy-combustion is today seen as a promising solution, since the exhaust effluent will have a higher CO_2 concentration.

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.

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 WO2022/002869, WO2022/238385, 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.

However, today, while the operation of PFRK in oxy-combustion seems to be a very promising solution, there remains uncertainties about feasibility and even no pilot kiln has been tested yet. therefore, the oxy-combustion operation while theoretically known and understood has also not yet been tested with respect to impact on lime quality and this technology appears still quite expensive for producing commodities products, despite the little required modifications to the kiln structure.

In view of the aforementioned, it is to be expected that PFRK operated in common combustion will remain the gold standard for a while.

However, as aforementioned, being able to concentrate the CO_2 in the exhaust effluent can yield to a better efficiency in CO_2 recovery in the fumes and reduce the CO_2 emission in the atmosphere.

There is therefore a need to provide a method to be carried out in PFRK under common combustion operation 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 can be industrially valorized while not operating in oxy-combustion.

To solve these problems, the present invention provides a method for calcining carbonate mineral stones in a parallel flow regenerative kiln (such as operating in common combustion) 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 introduced 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 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 :

- Upon said preheated carbonate mineral stones descending into said shaft, decarbonation of the preheated carbonate mineral stones 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,

- 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 a step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 20 to 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft from

- (i) the shaft in calcining mode or,
- (ii) from the shaft in preheating mode or,
- (iii) from both the shaft in calcining mode and the shaft in preheating mode with a predetermined amount x of heated cooling gas being extracted from the shaft in calcining mode and a predetermined amount y of heated cooling gas being extracted from the shaft in preheating mode with x+y being equal to the amount of extracted heated cooling gas, i.e. to the amount comprised

between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft.

As it can be seen the method according to the present invention comprises in standard operation, the steps of conducting the kiln where the carbonate mineral stones are loaded at the top of each shaft, then preheated in a preheating zone, calcined in a calcination zone with the production of a decarbonated calcined material and combustion fumes before being cooled with cooling gas in a cooling zone. The cooling step is accompanied by the formation of heated cooling gas by heat exchange, i.e. the cooling gas capture the heat from the calcined stones. After being cooled, the calcined material is discharged from the bottom of the shafts.

During the method according to the present invention, a exhaust effluent containing the combustion fumes is exhausted from the kiln and each shaft alternately works 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.

In the method according to the present invention, the calcining mode comprises a decarbonation of the preheated carbonate mineral stones upon descending into said shaft, with the release of combustion fumes descending co-currently in the shaft in calcination mode passing then through said connecting channel, toward the at least one shaft working in a preheating mode. The preheating mode comprises the preheating step of the loaded carbonate mineral stones by heat exchange with said fumes coming from the connecting channel, which is ascending and flows in counter-current through the loaded carbonate mineral stones, and the exhausting step of said combustion fumes as exhaust effluent at the top of said at least one shaft in preheating mode.

The method according to the present invention contemplates a step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 20 to 90 vol% of said heated cooling gas to avoid dilution of CO_2 in the exhaust effluent by the cooling gas, which allow to exit an exhaust effluent having a higher concentration in CO_2. This CO_2 can then be used or sequestered under favorable conditions, drastically decreasing the contribution of the kiln to the greenhouse effect.

The withdrawal outside of the kiln also allow to reduce the kiln pressure drop, which is most often the limiting factor for the production rate of a PFRK. Accordingly, a production increase can possibly be reached with the step of withdrawal of the cooling gas. The amount of cooling gas that is extracted is comprised between 20 and 90% with respect to the introduced amount of cooling gas from the same shaft and should be controlled to keep the kiln flue gas temperature above the dew point of about 60°C and is preferably set by security above 80°C.

The withdrawal step can be performed from any of the shaft (i.e. from the shaft in calcining mode or from the shaft in preheating mode) but can also be performed from both the shaft in calcining mode and the shaft in preheating mode with a predetermined amount x of heated cooling gas being extracted from the shaft in calcining mode and a predetermined amount y of heated cooling gas being extracted from the shaft in preheating mode with x+y being equal to the amount of extracted heated cooling gas, i.e. to the amount comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft. As it can be seen, the amount of extracted cooling gas should not necessarily be the same in the shaft in calcining mode and in the shaft in preheating mode. Further, for simplification, one may prefer to extract the heated cooling gas from only one shaft.

In a preferred embodiment, the step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 20 to 90 vol% of said heated cooling gas is a step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 30 to 80 vol%, preferably from 35 to 75 vol%, more preferably from 40 to 70 vol%, even more preferably from 45 to 65 vol% of said heated cooling gas, so the amount of extracted heated cooling gas is comprised between 30 and 80 vol%, preferably between 35 and 75 vol%, more preferably between 40 and 70 vol%, even more preferably between 45 and 65 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft, said step of withdrawal of heated cooling gas is preferably controlled by the temperature of the exhaust effluent exhausted at the top of the shaft in preheating mode in such a way that said amount of extracted heated cooling gas is continuously controlled, preferably continuously modulated to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

In a preferred embodiment according the present invention, when said extracted heated cooling gas is extracted from the shaft in calcining mode, said extracted heated cooling gas is extracted from 50 to 100% by volume on dry gas basis relative to the introduced cooling gas in the same shaft 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 gas in the same shaft through a central collector element in fluid communication with said cooling zone, and when said extracted heated cooling gas is extracted from the shaft in preheating mode, said extracted heated cooling gas is extracted from 0 to 50% by volume on dry gas basis relative to the introduced cooling gas in the same shaft 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 gas in the same shaft through a central collector element in fluid communication with said cooling zone.

According to the present invention, preferably, 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.

It is advantageous according to the present invention for the heated cooling gas to be extracted at different location depending on 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, due to its momentum, the exhaust effluent which is rich in CO_2 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 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%)I by volume on dry gas basis relative to the volume of the introduced cooling gas 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 gas 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 gas 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 volume of the introduced cooling gas 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 end 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, said extracted heated cooling gas is extracted from the shaft in calcining mode, the extracted 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 gas in the same shaft 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 gas in the same shaft through said central collector element and when said

extracted heated cooling gas is extracted from the shaft in preheating mode, the extracted 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 gas in the same shaft 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 gas in the same shaft from 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 calcination 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 according to the present invention, the method further comprises injection of combustion air and fuel in the calcining shaft, preferably in the calcination zone, to perform the decarbonation of preheated carbonate mineral stones through a combustion of fuel, the combustion fumes comprising CO_2 from the decarbonation of carbonate mineral stones and from combustion of fuel.

Preferably, the combustion air is injected in excess with respect to the stoichiometric conditions for fuel combustion, for example with an excess factor of at least 1.05, preferably 1.1.

As it can be seen, the method according to the present invention is carried out in a kiln working in common operation, meaning with combustion of fuel in presence of combustion air. Under common operation, it has appeared that even if the (released) fumes can't be as concentrated in CO_2 as under oxy-combustion operation, the valorisation of the CO_2 in the fumes is nevertheless higher than under common

condition facilitating therefore the recovery of this latter. Further as the production rate of the kiln is improved due to the reduced pressure drop, the yield of the method is enough to provide the profitability for the CO_2 recovery.

According to said preferred embodiment, preferably said combustion of fuel 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 may be carried out using either air or a collected portion of exhaust effluent discharged from the kiln, or using another source of CO_2 as a carrier gas or using another source of gas as a carrier gas, such as combustion air.

According to said preferred embodiment, preferably, a portion of the exhaust effluent discharged from the kiln may be introduced in lances for fuel injection or in an outer envelope enclosing lances for fuel injection for cooling said lances in the shaft in preheating mode.

According to said preferred embodiment, preferably, the exhaust effluent is partially or fully collected in at least one buffer after said exhausting step or in a storage tank or first in one buffer and then in a storage tank, the buffer and the storage tank being located in series or first in a storage tank and then in a buffer, the storage tank and the buffer being located in series.

In one embodiment, the method according to the present invention 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. 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 a preferred embodiment, said cooling gas is air.

In another 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 and/or concentration for producing a substantially pure CO_2 gas, before or after the step of collecting the exhaust effluent in said buffer, preferably after.

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 for implementing the method according to anyone of the preceding claims, comprising

- at least two shafts, interconnected by a connecting channel, having each a preheating zone, a combustion zone and a cooling zone,
- each of said shafts comprising, in the on or off position,
- at least one fuel supply device,
- at least one supply opening for combustion air,
- 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 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, 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 comprises a cross-over channel that connects the peripheral channels arranged around each shaft so as to allow a transfer of gas,

said kiln being characterized in that the kiln is further provided with a cooling gas extraction device connected to and controlling a heated cooling gas extraction system located below the connecting channel and provided to withdraw cooling gas below the connecting channel, said cooling gas extraction device having an inlet to receive a signal from a temperature probe located in the exhaust effluent discharge duct and being provided to control said heated cooling gas extraction system to output an amount of extracted heated cooling gas by the heated cooling gas extraction system between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over at least one cycle of the kiln, i.e. a sequence of at least one calcining mode, inversion and preheating mode for each shaft and to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

In a preferred embodiment of the kiln according to the present invention, the heated cooling gas extraction device is connected to a modulating valve located on said heated cooling gas extraction system and modulate its opening degree to withdraw by the heated cooling gas extraction system an amount of heated cooling gas

comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft continuously over said at least one cycle of the kiln, in order to continuously keep the exhaust effluent temperature close to said threshold. This can be for example performed by continuously having the opening of the valve modulated or based on a predefined opening of the valve, said predefined opening of the valve being modulated based on the exhaust effluent temperature of at least the previous cycle

In one alternative embodiment of the kiln according to the present invention, said heated cooling gas extraction system has an "open and off" position means provided to shift the heated cooling gas extraction system from an open-position to an off-position and vice versa, said open-position and off-position being actioned by said cooling gas extraction device upon a signal from a temperature probe located in the exhaust effluent discharge in such a way that the temperature of the exhaust effluent will remain in a limited range above said threshold, said cooling gas extraction device being further provided to control the flow rate of the extraction of heated cooling gas in the open-position of the heated cooling gas extraction system in such a way the amount of extracted heated cooling gas is comprised between 20 to 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over said at least one cycle.

According to the present invention, the amount of extracted heated cooling gas is for example comprised between 30 and 80 vol%, preferably between 35 and 75 vol%, more preferably between 40 and 70 vol%, even more preferably between 45 and 65 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over said at least one cycle and said threshold value is of at least 60°C, preferably above 70°C, more preferably above 80°C.

In a preferred embodiment, in the kiln according the present invention, the heated cooling gas extraction system is in fluid communication with the cooling zone of at least one shaft and is located on

- (i) the shaft in calcining mode or,
- (ii) the shaft in preheating mode or,
- (iii) has a first and second heated cooling gas extraction system, respectively in fluid communication with the shaft in calcining mode and the shaft in preheating mode, both first and second heated cooling gas extraction system being controlled by the cooling gas extraction device to output a predetermined amount x of heated cooling gas being extracted from the shaft in calcining mode and a predetermined amount y of heated cooling gas being extracted from the shaft in preheating mode with x+y being equal to the amount of extracted heated cooling gas, i.e. to the amount comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft.

In a further preferred embodiment, the heated cooling gas extraction system is either,

(i) below the connecting channel, a collector peripheral ring connected with a first extracting element being a part of the cooling gas extraction device so as to allow heated cooling gas to be removed from the kiln, said first extracting element being controlled by a first control means of the cooling gas extraction device, or

(ii) below the connecting channel, more preferably at the bottom of the shaft, a central collector element connected with a second extracting element being a part of the cooling gas extraction device so as to allow heated cooling gas to be removed from the kiln, said second extracting

element being controlled by a second control means of the cooling gas extraction device, said first control means and said second control means being preferably synchronized with said reversing system, or

(iii) below the connecting channel, a collector peripheral ring connected with a first extracting element being a part of the cooling gas extraction device so as to allow heated cooling gas to be removed from the kiln, said first extracting element being controlled by a first control means of the cooling gas extraction device, and below the connecting channel, more preferably at the bottom of the shaft, a central collector element connected with a second extracting element being a part of the cooling gas extraction device so as to allow heated cooling gas to be removed from the kiln, said second extracting element being controlled by a second control means of the cooling gas extraction device, said first control means and said second control means being synchronized with said reversing system.

Advantageously, 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 yet a further preferred embodiment, 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.

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.

In a preferred embodiment of the kiln according to the present invention, the exit of exhaust effluent is connected to at least one device chosen in the group comprising a filter, a gas cooler, a heat exchanger, a buffer, a storage vessel, a purification unit to purify CO_2 contained in the exhaust effluent, a concentration device to concentrate the CO_2 contained in the exhaust effluent, a pressurization device to pressurize the exhaust effluent, such as for producing liquid CO_2, a gas heater, a scrubber, a separating element to divide exhaust gas effluent into at least a flow connected to the chimney and a flow connected to another device for treating the exhaust effluent and their combination.

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 exhaust effluent.

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.

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.

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 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, 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 can supplied by the carbonate stones one or more times. The opening 6 for supplying combustion air is closed. However, the supply duct 7 for the cooling gas remain in the open position. The unloading equipment 24 continues to discharge lime from the kiln through outlet 8. 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's such as filters. In the shaft in calcination 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 calcination 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 cooling , preferably cooling air is extracted below the connecting channel, by means of a collector peripheral ring 25 connected with a first extracting element 26 being a part of the cooling gas extraction device 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 of the cooling gas extraction device.

The collector peripheral ring has been shown on the two shafts of the illustrated kiln, but it can be only present on one shaft. The collector peripheral ring 25 can be also present on the two shafts 1,2 but only working when the shaft is in calcining mode. The collector peripheral ring 25 can alternatively be present on the two shafts 1,2 but only working when the shaft is in preheating mode. In the two latter cases, the first extracting element 26 will be activated by the inversion means 16.

The heated cooling gas extraction system on figure 2 is accordingly the collector peripheral ring 25 connected to and controlled by the first extraction means 26 of the cooling gas extraction device.

The cooling gas extraction device has an input to receive a signal from a temperature probe located in the exhaust effluent discharge duct and being provided to control said heated cooling gas extraction

system to output an amount of extracted heated cooling gas by the heated cooling gas extraction system between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over at least one cycle of the kiln, i.e. a sequence of at least one calcining mode, inversion and preheating mode for each shaft and to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

Further, In one embodiment, the heated cooling gas extraction device (first extraction means 26) is connected to a modulating valve located on said heated cooling gas extraction system and modulate its opening degree to withdraw by the heated cooling gas extraction system an amount of heated cooling gas comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft continuously over said at least one cycle of the kiln

In another embodiment, the heated cooling gas extraction system has an "open and off" position means provided to shift the heated cooling gas extraction system from an open-position to an off-position and vice versa, said open-position and off-position being actioned by said cooling gas extraction device upon a signal from a temperature probe located in the exhaust effluent discharge in such a way that the temperature of the exhaust effluent will remain in a limited range above said threshold. The cooling gas extraction device (first extraction means 26) is further provided to control the flow rate of the extraction of heated cooling gas in the "open" position of the heated cooling gas extraction system in such a way the amount of extracted heated cooling gas is comprised between 20 to 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft.

Preferably, the amount of extracted heated cooling gas is for example comprised between 30 and 80 vol%, preferably between 35 and

75 vol%, more preferably between 40 and 70 vol%, even more preferably between 45 and 65 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft and said threshold value is of at least 60°C, preferably above 70°C, more preferably above 80°C.

The kiln according to the present invention can optionally also comprise a heat exchanger 17, fed by the extracted heated cooling gas, for example to preheat the combustion air or the fuel 9.

Figure 3 shows an alternative embodiment of the present invention where the where the cooling gas is extracted below the connecting channel, preferably at the bottom of the shaft, by means of a central collecting element 27 connected with a second extracting element 28 being a part of the cooling gas extraction device 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 of the cooling gas extraction device.

Central collecting element 27 has been shown on the two shafts of the illustrated kiln, but it can be only present on one shaft. The central collecting element 27 can be also present on the two shafts but only working when the shaft is in calcining mode. The central collecting element 27 can alternatively be present on the two shafts but only working when the shaft is in preheating mode. In the two latter cases, the second extracting element 26 will be activated by the inversion means 16.

The heated cooling gas extraction system on figure 3 is accordingly the central collecting element 27 connected to and controlled by the second extraction means 28 of the cooling gas extraction device.

The heated cooling extraction device has an inlet to receive a signal from a temperature probe located in the exhaust effluent discharge duct and being provided to control said heated cooling gas extraction system to output an amount of extracted heated cooling gas

by the heated cooling gas extraction system between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over at least one cycle of the kiln, i.e. a sequence of at least one calcining mode, inversion and preheating mode for each shaft and to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

Further, In one embodiment, the heated cooling gas extraction device (second extraction means 28) is connected to a modulating valve located on said heated cooling gas extraction system and modulate its opening degree to withdraw by the heated cooling gas extraction system an amount of heated cooling gas comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft continuously over said at least one cycle of the kiln

In another embodiment, the central collecting element 27 of each shaft, forming the cooling gas extraction system have each an "open and off" position means provided to shift respectively the central collecting element 27 of each shaft from an open-position to an off-position and vice versa, said off-position. The open-position and off-position being actioned by said cooling gas extraction device upon a signal from a temperature probe located in the exhaust effluent discharge in such a way that the temperature of the exhaust effluent will remain in a limited range above said threshold. Preferably, the amount of extracted heated cooling gas is for example comprised between 30 and 80 vol%, preferably between 35 and 75 vol%, more preferably between 40 and 70 vol%, even more preferably between 45 and 65 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft and said threshold value is of at least 60°C, preferably above 70°C, more preferably above 80°C.

The kiln according to the present invention can optionally also comprise a heat exchanger 17, fed by the extracted heated cooling gas, for example to preheat the combustion air or the fuel 9.

Figure 4 shows another alternative embodiment of the present invention where the shafts are both provided with a collector peripheral ring 25 connected to a first extracting element 26 and a central collecting element 27 connected with a second extracting element 28 to extract the cooling gas which has been heated by heat exchange with the descending stones. The heated cooling gas extraction system comprises accordingly the collector peripheral ring 25 and the central collecting element 27 while the cooling gas extraction device comprises the first extracting element 26 and the second extracting element 28.

The first extracting element 26 and the second extracting element 28 have each an inlet to receive a signal from a temperature probe located in the exhaust effluent discharge duct 14 and being provided to control the central collecting element 27 and the collector peripheral ring 25 of each shaft to output an amount of extracted heated cooling gas by the heated cooling gas extraction system between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over at least one cycle of the kiln, i.e. a sequence of at least one calcining mode, inversion and preheating mode for each shaft and to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

Further, In one embodiment, the first extraction means 26 and second extraction means 28 are each connected to a modulating valve located on the central collecting element 27 and on the collector peripheral ring 25 of each shaft and modulate its opening degree to withdraw by them an amount of heated cooling gas comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced

cooling gas in the same shaft continuously over said at least one cycle of the kiln.

In another embodiment, the central collecting element 27 and the collector peripheral ring 25 of each shaft, forming the cooling gas extraction system have each an "open and off" position means provided to shift respectively the central collecting element 27 and the collector peripheral ring 25 of each shaft from an open-position to an off-position and vice versa, said off-position. The open-position and off-position being actioned by said cooling gas extraction device upon a signal from a temperature probe located in the exhaust effluent discharge in such a way that the temperature of the exhaust effluent will remain in a limited range above said threshold. Preferably, the amount of extracted heated cooling gas is for example comprised between 30 and 80 vol%, preferably between 35 and 75 vol%, more preferably between 40 and 70 vol%, even more preferably between 45 and 65 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft and said threshold value is of at least 60°C, preferably above 70°C, more preferably above 80°C.

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 of heated cooling gas relative to the introduced cooling gas in the same shaft 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 of heated cooling gas relative to the introduced cooling gas in the same shaft 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 of heated cooling gas relative to the introduced cooling gas in the same shaft 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 of heated cooling gas relative to the introduced cooling gas in the same shaft 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 combustion air or the fuel 9, through the heat exchanger 17 or 18 or 19.

The present invention was illustrated with some embodiments but of course other combinations are possible such as for example a combination of the embodiment of figure 2 and the embodiment of figure 3.

Examples.-

Comparative example.-

A parallel flow regenerative kiln according to the present invention having a capacity of 350 TPD of calcined mineral stones, where fuel (lignite) is burned with combustion air fed at a flow rate of 15420 Nm^3/h, (i.e. in common combustion conditions) has been numerically modelized. The combustion was performed in excess of air (excess air ratio 1.2).

The kiln has a specific heat consumption of 3.4 GJ/ton of quicklime. Cooling air is introduced at a specific flow rate of 9050 Nm^3/h and the flow rate of the exhaust effluent is 31000 Nm^3/h. The temperature of the exhaust effluent at the exit of the preheating shaft is 130°C.The kiln pressure drop was 210 mbar.

Table 1.- exhaust effluent composition

CO_2 (dry basis)	25.8 vol%
N_2 (dry basis)	65.8 vol%
O_2 (dry basis)	8.4 vol%
Moisture	4.4 vol%

Example.-

The same parallel flow regenerative kiln as comparative example has been numerically modelized, where fuel (lignite) is burned with combustion air fed at a flow rate of 16700 Nm^3/h, (i.e. in common combustion conditions) has been numerically modelized. The combustion was performed in excess of air (excess air ratio 1.2)..

The kiln now has a specific heat consumption of 3.7 GJ/ton of mineral stones to compensate the loss of heat with the extracted cooling air. Cooling air is introduced at a specific flow rate of 9050 Nm^3/h and the flow rate of the exhaust effluent is 28100 Nm^3/h. 50% of the heated cooling air with respect to the amount of cooling air introduced in the same shaft

is extracted. The temperature of the exhaust effluent at the exit of the preheating shaft is 88°C.The kiln pressure drop was 165 mbar.

Table 2.- exhaust effluent composition

CO_2 (dry basis)	30.0 vol%
N_2 (dry basis)	64.0 vol%
O_2 (dry basis)	6.0 vol%
Moisture	5.3 vol%

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 :
    - Upon said preheated carbonate mineral stones descending into said shaft, decarbonation of the preheated carbonate mineral stones 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,
- said preheating mode comprising :

- said preheating step of the loaded carbonate mineral stones by heat exchange with said combustion fumes (11) 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 fumes as exhaust effluent at the top of said at least one shaft in preheating mode,

characterized in that said method further comprises a step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 20 to 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft from

- (i) the shaft in calcining mode or,
- (ii) from the shaft in preheating mode or,
- (iii) from both the shaft in calcining mode and the shaft in preheating mode with a predetermined amount x of heated cooling gas being extracted from the shaft in calcining mode and a predetermined amount y of heated cooling gas being extracted from the shaft in preheating mode with x+y being equal to the amount of extracted heated cooling gas, i.e. to the amount comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft.

2. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to claim 1, wherein the step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 20 to 90 vol% of said heated cooling gas is a step of withdrawal outside of the kiln of an extracted heated cooling gas formed by from 30 to 80 vol%, preferably from 35 to 75 vol%, more preferably from 40 to 70 vol%, even more preferably from 45 to 65 vol% of said heated cooling gas, so the amount of extracted heated cooling gas is comprised between 30

and 80 vol%, preferably between 35 and 75 vol%, more preferably between 40 and 70 vol%, even more preferably between 45 and 65 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft, said step of withdrawal of heated cooling gas is preferably controlled by the temperature of the exhaust effluent exhausted at the top of the shaft in preheating mode in such a way that said amount of extracted heated cooling gas is continuously controlled, preferably continuously modulated to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

3. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to claim 1 or claim 2, wherein when said extracted heated cooling gas is extracted from the shaft in calcining mode, said extracted heated cooling gas is extracted from 50 to 100% by volume on dry gas basis relative to the introduced cooling gas in the same shaft through a collector peripheral ring (25) in fluid connection with the cooling zone, at a level located below the connecting channel (3, 13), and from 0 to 50% by volume on dry gas basis relative to the introduced cooling gas in the same shaft through a central collector element (27) in fluid communication with said cooling zone, and when said extracted heated cooling gas is extracted from the shaft in preheating mode, said extracted heated cooling gas is extracted from 0 to 50% by volume on dry gas basis relative to the introduced cooling gas in the same shaft through a collector peripheral ring (25) in fluid connection with the cooling zone, at a level located below the connecting channel (3, 13) and from 50 to 100% by volume on dry gas basis relative to the introduced cooling gas in the same shaft through a central collector element (27) in fluid communication with said cooling zone.

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

said extracted heated cooling gas is extracted from the shaft in calcining mode, the extracted 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 gas in the same shaft 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 gas in the same shaft through said central collector element (27) and when said extracted heated cooling gas is extracted from the shaft in preheating mode, the extracted 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 gas in the same shaft 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 gas in the same shaft from through said central collector element (27).

5. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the claims 1 to 4, further comprising injection of combustion air and fuel in the calcining shaft, preferably in the calcination zone, to perform the decarbonation of preheated carbonate mineral stones through a combustion of fuel, the combustion fumes comprising CO_2 from the decarbonation of carbonate mineral stones and from combustion of fuel.

6. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to claim 5, wherein said combustion of fuel 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 air or a collected portion of exhaust effluent discharged from the kiln, or using another source of CO_2 as a carrier gas or using another source of gas as a carrier gas, such as combustion air.

7. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to claim 5 or claim 6, wherein a portion of the exhaust effluent discharged from the kiln is introduced in lances (4) for fuel injection or in an outer envelope enclosing lances(4) for fuel injection for cooling said lances (4) in the shaft in preheating mode.

8. Method for calcining carbonate mineral stones in a parallel flow regenerative kiln according to any of the claims 1 to 7, wherein the exhaust effluent is partially or fully collected in at least one buffer after said exhausting step.

9. 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 or only of the shaft working in the calcining mode, or only in the shaft working in the preheating mode.

10. 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.

11. 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 and/or concentration for producing a substantially pure CO_2 gas, before or after the step of collecting the exhaust effluent in said buffer, preferably after.

12. 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), having each a preheating zone, a combustion zone and a cooling zone,
- 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 combustion air,

- 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 (1, 2),

- a 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, 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 said connecting channel (3, 13) is 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 the kiln is further provided with a cooling gas extraction device connected to and controlling a heated cooling gas extraction system located below the connecting channel, and provided to withdraw cooling gas below the connecting channel, said cooling gas extraction device having an inlet to receive a signal from a temperature probe located in the exhaust effluent discharge duct and being provided to control said heated cooling gas extraction system to output an amount of extracted heated cooling gas by the heated

cooling gas extraction system between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over at least one cycle of the kiln, i.e. a sequence of at least one calcining mode, inversion and preheating mode for each shaft and to maintain the temperature of the exhaust effluent above a threshold value of at least 60°C, preferably above 70°C, more preferably above 80°C.

13. Parallel-flow regenerative kiln according to claim 12, wherein the heated cooling gas extraction device is connected to a modulating valve located on said heated cooling gas extraction system and modulate its opening degree to withdraw by the heated cooling gas extraction system an amount of heated cooling gas comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft continuously over said at least one cycle of the kiln.

14. Parallel-flow regenerative kiln according to claim 12, wherein said heated cooling gas extraction system has an "open and off" position means provided to shift the heated cooling gas extraction system from an open-position to an off-position and vice versa, , said open-position and off-position being actioned by said cooling gas extraction device upon a signal from a temperature probe located in the exhaust effluent discharge in such a way that the temperature of the exhaust effluent will remain in a limited range above said threshold, said cooling gas extraction device being further provided to control the flow rate of the extraction of heated cooling gas in the open-position of the heated cooling gas extraction system in such a way the amount of extracted heated cooling gas is comprised between 20 to 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft over said at least one cycle.

15. Parallel-flow regenerative kiln according to any of the claims 12 to 14, wherein the heated cooling gas extraction system is in fluid

communication with the cooling zone of at least one shaft and is located on

- (i) the shaft in calcining mode or,
- (ii) the shaft in preheating mode or,
- (iii) has a first and second heated cooling gas extraction system, respectively in fluid communication with the shaft in calcining mode and the shaft in preheating mode, both first and second heated cooling gas extraction system being controlled by the cooling gas extraction device to output a predetermined amount x of heated cooling gas being extracted from the shaft in calcining mode and a predetermined amount y of heated cooling gas being extracted from the shaft in preheating mode with x+y being equal to the amount of extracted heated cooling gas, i.e. to the amount comprised between 20 and 90 vol% of said heated cooling gas relative to the introduced cooling gas in the same shaft.

16. Parallel-flow regenerative kiln according to any of the claims 12 to 15, wherein the heated cooling gas extraction system is either, (i) below the connecting channel (3, 13), a collector peripheral ring (25) connected with a first extracting element (26) being a part of the cooling gas extraction device 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 of the cooling gas extraction device, or (ii) below the connecting channel, more preferably at the bottom of the shaft, a central collector element (27) connected with a second extracting element (28) being a part of the cooling gas extraction device 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 of the cooling gas extraction device, said first control means and

said second control means being preferably synchronized with said reversing system, or

(iii) below the connecting channel (3, 13), a collector peripheral ring (25) connected with a first extracting element (26) being a part of the cooling gas extraction device 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 of the cooling gas extraction device, and below the connecting channel (3, 13), more preferably at the bottom of the shaft (1, 2), a central collector element (27) connected with a second extracting element (28) being a part of the cooling gas extraction device 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 of the cooling gas extraction device, said first control means and said second control means being synchronized with said reversing system (16).

17. Parallel-flow regenerative kiln according to claim 16, 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.

18. Parallel-flow regenerative kiln according to any of the claims 16 or 17, wherein said central collector element (27) (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 (3, 13), 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.

19. Parallel-flow regenerative kiln according to claim 18, wherein 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.

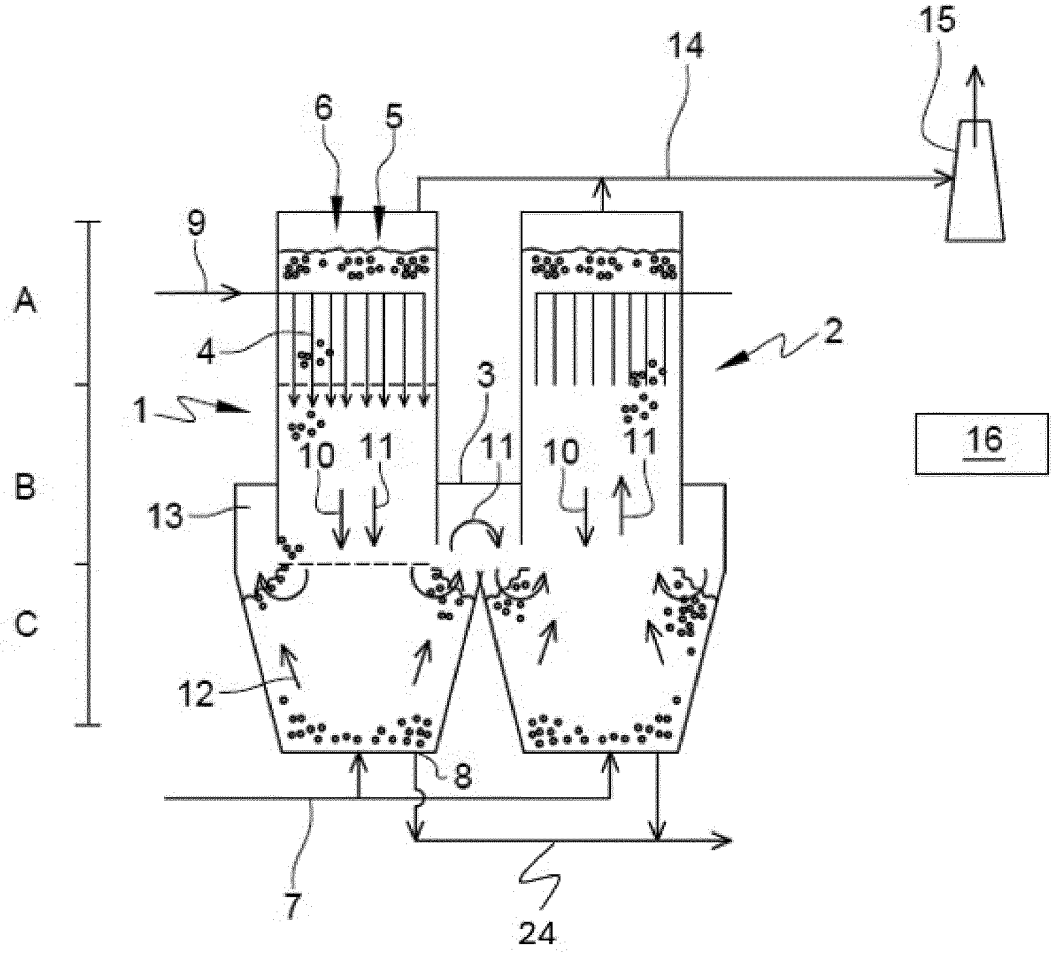


Fig. 1

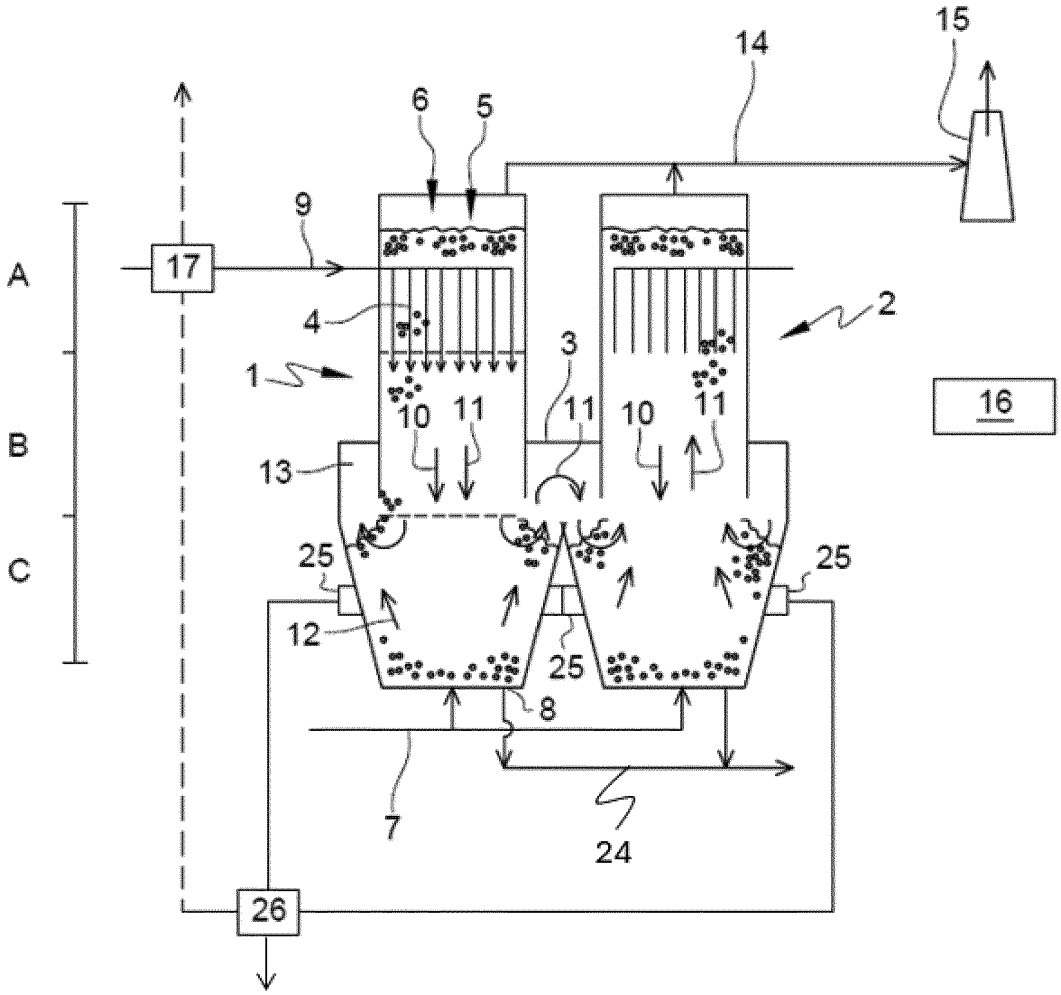


Fig. 2

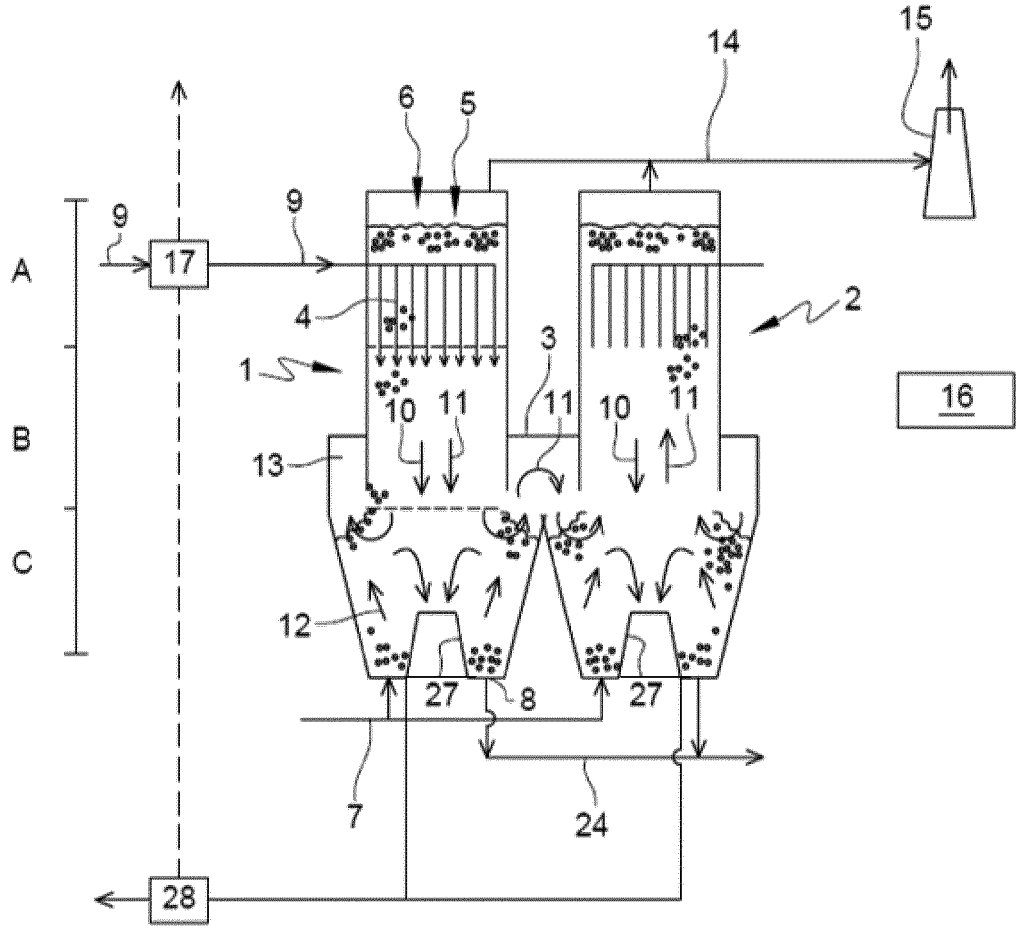


Fig. 3

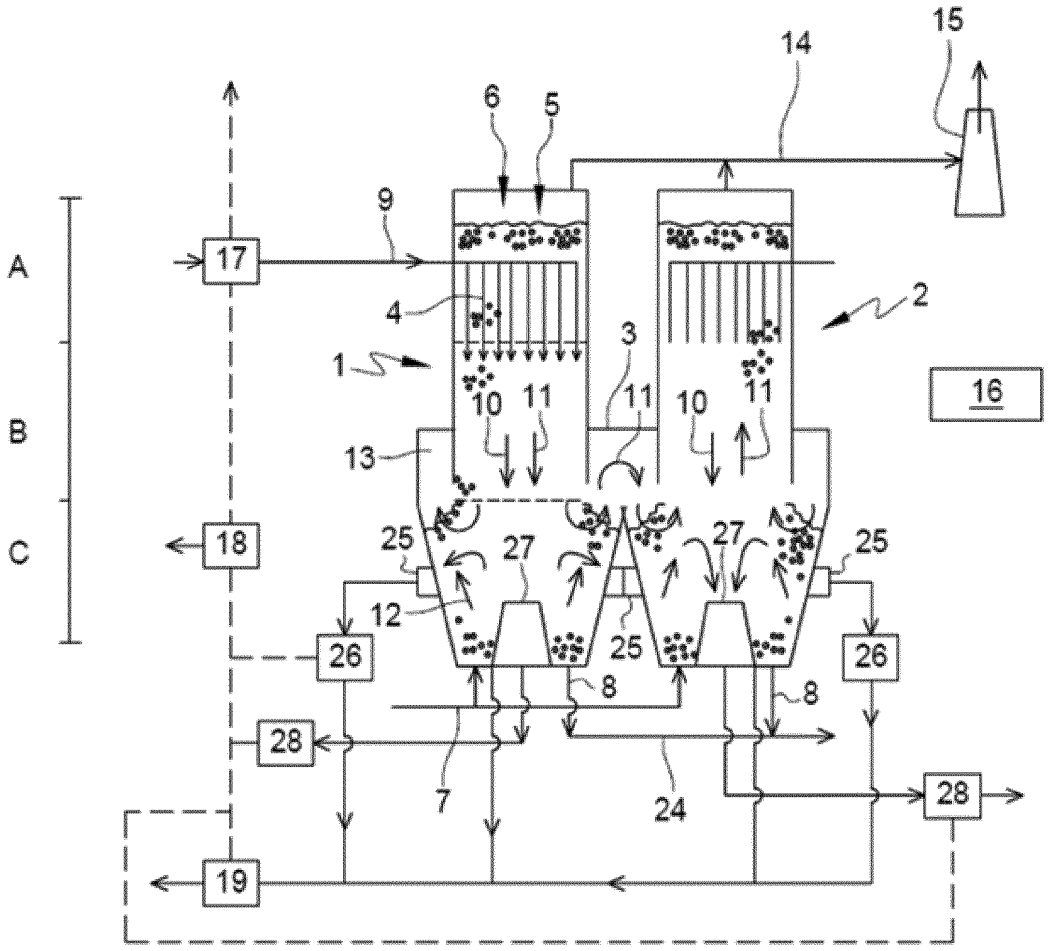


Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/063973

A. CLASSIFICATION OF SUBJECT MATTER

INV. F27B1/00 C04B2/12 F27B1/02 F27B1/22 F27B1/26
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

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	EP 4 175 920 B1 (LHOIST RECH ET DEVELOPPEMENT SA [BE]) 24 April 2024 (2024-04-24) figure 4 paragraph [0001] - paragraph [0009] paragraph [0014] - paragraph [0024] paragraph [0029] - paragraph [0054] -----	1-19
X	WO 2022/238385 A1 (TECFORLIME [BE]) 17 November 2022 (2022-11-17) figures 1-22 paragraph [0001] paragraph [0021] - paragraph [0024] paragraph [0029] -----	1-19

-/--

[x] Further documents are listed in the continuation of Box C.

[x] 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
4 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	Jung, Régis

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/063973

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2022/229118 A1 (MAERZ OFENBAU [CH]; THYSSENKRUPP IND SOLUTIONS AG [DE] ET AL.) 3 November 2022 (2022-11-03) figures 1-5 page 1, line 1 - page 2, line 8 page 14, line 27 - page 29, line 35 -----	1-19
X	DE 29 27 834 A1 (MAERZ OFENBAU) 27 March 1980 (1980-03-27) figures 1-4 page 1, line 1 - line 5 page 3, line 6 - page 10, line 10 -----	1-19

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/063973

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 4175920 B1	24-04-2024	BR 112022025510 A2	17-01-2023
		CA 3183046 A1	06-01-2022
		CN 115803301 A	14-03-2023
		EP 4175920 A1	10-05-2023
		EP 4282842 A2	29-11-2023
		EP 4324799 A2	21-02-2024
		EP 4324800 A2	21-02-2024
		EP 4397639 A2	10-07-2024
		ES 2983795 T3	24-10-2024
		FI 4175920 T3	23-07-2024
		HR P20240989 T1	25-10-2024
		HU E067303 T2	28-10-2024
		JP 2023533226 A	02-08-2023
		PL 4175920 T3	02-09-2024
		PT 4175920 T	17-07-2024
		RS 65738 B1	30-08-2024
		SI 4175920 T1	30-09-2024
		US 2023227353 A1	20-07-2023
		WO 2022002869 A1	06-01-2022
WO 2022238385 A1	17-11-2022	AU 2022275001 A1	02-11-2023
		BR 112023023566 A2	12-03-2024
		CA 3218534 A1	17-11-2022
		EP 4337621 A1	20-03-2024
		US 2024254043 A1	01-08-2024
		WO 2022238385 A1	17-11-2022
WO 2022229118 A1	03-11-2022	BR 112023022468 A2	15-02-2024
		EP 4182622 A1	24-05-2023
		EP 4330614 A1	06-03-2024
		ES 2969644 T3	21-05-2024
		PL 4182622 T3	06-05-2024
		US 2024361074 A1	31-10-2024
		WO 2022229118 A1	03-11-2022
		WO 2022229119 A1	03-11-2022
DE 2927834 A1	27-03-1980	AT 372519 B	25-10-1983
		CA 1124513 A	01-06-1982
		CH 637760 A5	15-08-1983
		DE 2927834 A1	27-03-1980
		FR 2436346 A1	11-04-1980
		JP S5539300 A	19-03-1980
		JP S5816932 B2	04-04-1983