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MENETELMÄ MINERAALIKIVEN KALSINOIMISEKSI REGENERATIIVISESSA, SAMANSUUNTAISIIN VIRTOIHIN PERUSTUVASSA PYSTYKUILU-UUNISSA JA KÄYTETTÄVÄ UUNI

METHOD FOR CALCINING MINERAL ROCK IN A REGENERATIVE PARALLEL-FLOW VERTICAL SHAFT FURNACE, AND FURNACE USED

METHOD FOR CALCINING MINERAL ROCK IN A REGENERATIVE PARALLEL-FLOW VERTICAL SHAFT FURNACE AND FURNACE USED

The present invention relates to a method for calcining carbonate mineral rock in a regenerative parallel-flow vertical shaft furnace and to the furnace used.

The regenerative parallel-flow vertical shaft furnace or Parallel Flow Regenerative Kiln (PFRK) has an energy efficiency of 85% to 90%; it is the highest in the lime sector, even in the entire energy-intensive cement, steel and glass industry. In Europe, 60% of the lime is produced in this type of furnace. This proportion is set to increase in Europe and worldwide, taking into account the roadmaps for energy and ecological transition.

The 'PFRK' furnace is a vertical double-shaft furnace where the fuel is injected alternately in one shaft then in another for approximately 10 to 15 minutes with a stop period between cycles of approximately 1 to 2 minutes to reverse the air and fuel circuits. This is the "reversing" period. The two shafts are connected via a connecting flue. When a shaft is combusting (firing mode), the hot combustion fumes pass through the connecting flue (gas transfer channel) and give a portion of their heat to the mineral rock to be calcined in order to preheat it in the other shaft in regeneration or preheating mode. The shafts of the PFRK furnace are either cylindrical or rectangular. In some cases, there are three shafts, two in preheating mode and one in firing mode. The problems and solutions outlined below are valid for all PFRK furnace geometries.

The method used in these known furnaces comprises, in production mode:

- loading the carbonate mineral rock at the top of the furnace,
- preheating said rock,
- firing said rock with the decarbonation thereof to calcined material,
- cooling the calcined material using cooling air, and
- unloading the calcined material at the bottom of the shafts,
- each shaft operating alternately in firing mode and in preheating mode, one shaft being in firing mode for a predetermined time period while at least one other shaft is in preheating mode and vice-versa,
- the firing mode comprising:
  said loading of carbonate mineral rock at the top of the shaft in firing mode,
  in the presence of said preheated carbonate mineral rock descending into this shaft, combusting fuel in the presence of oxygen so as to obtain said firing of this rock and

the decarbonation thereof into calcined material with the release of combustion fumes in the form of a gaseous stream descending co-currently in the shaft in firing mode, and said gaseous stream containing these combustion fumes moving from the shaft in firing mode to said at least one shaft in preheating mode using said gas transfer channel,

- the preheating mode comprising:
  said preheating of the loaded carbonate mineral rock via heat exchange with the gaseous stream containing the combustion fumes, from the gas transfer channel, which is ascending in said at least one shaft in preheating mode counter-currently to said loaded carbonate mineral rock, and
  discharging a gaseous effluent based on the gaseous stream containing the combustion fumes from the furnace, at the top of said at least one shaft in preheating mode.

Within the meaning of the present invention, carbonate mineral rock, in particular, means limestone rock, dolomite rock and/or magnesite, which calcine respectively into quicklime, calcined dolomite and/or magnesia. The equation for the calcination of limestone to lime is as follows:

$CaCO_3$ (solid) + heat $\longleftrightarrow$ 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.

Therefore, during this process, the initial limestone or dolomite rock releases a large volume of CO_2 during the calcination thereof into lime or dolomite. Moreover, high temperatures must be reached to carry out this calcination and therefore fuels must be burned which, in turn, causes a large amount of CO_2 to be released. Overall, calcination methods have the disadvantage of actively contributing to the greenhouse effect.

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

To capture this CO_2, it may be considered to use the method of abatement by chemical solvent called "amines", which is the most widespread technique applied to the furnace fumes at the end of the line, after the dust collection filter. But the cyclical feature of the PFRK furnace with a furnace stop of 1 to 2 minutes every 10 to 15 minutes is incompatible with this technique, which is also very costly and involves a solvent that is not sustainable in terms of environmental legislation.

To be able to capture the CO_2 emitted in a PFRK furnace, replacing 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 firing mode has already been proposed in the method used (see CN105000811). JP2002060254 describes also a recycling of the combustion fumes as cooling air.

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 reform $CaCO_3$. On the other hand, using pure oxygen at the top of the furnace poses serious problems in terms of material compatibility 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 already been discussed in the patent application US2020/0048146.

It should also be noted that the cooling air in the PFRK furnace, in contrast to the rotary furnace, for example, does not have a direct impact on combustion and the calcination process in the shaft in firing mode. It has no expected effect on the quality of the product.

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

The present invention aims to at least partially remedy the problem of significant CO_2 emissions into the atmosphere from PFRK-type furnaces, without changing the cyclical operation thereof and with few or no changes to the structure thereof. It also aims to make it possible to capture the CO_2 present in the gaseous effluents emitted by the furnace.

To solve this problem, the present invention has provided a method for calcining mineral rock in a regenerative parallel-flow vertical shaft furnace as mentioned at the beginning, this method being characterized in that said combustion of fuel occurs in presence of oxygen excess with respect to the stoichiometric needs and further comprising:

- collecting a portion of the gaseous effluent discharged from the furnace,

- forming an oxidising mixture by mixing this collected portion of the gaseous effluent discharged from the furnace with concentrated dioxygen, and
- introducing this oxidising mixture at the top of the shaft in firing mode so as to ensure said fuel combustion in the presence of oxygen,

  the gaseous effluent discharged from the furnace having a high concentration of CO_2.

Fuel combustion in concentrated dioxygen would result in flame temperatures that are too high for the usual furnace equipment. It is also provided, according to the invention, to collect a portion of the gaseous effluent rich in CO_2 and to mix it with the dioxygen. Instead of a usual oxidant formed from the $O_2 + N_2$ mixture of air, a mixture of $O_2 + CO_2$ at an appropriate flame temperature is thus obtained.

Fuel combustion in dioxygen results in the gaseous stream containing the combustion fumes and in the calcination of the carbonate rock. This produces mainly CO_2 with some impurities, present as traces in the fuel and in the material to be calcined, and some oxygen not used up by the fuel combustion. Naturally, these combustion fumes also contain the CO_2 supplied to the oxidising mixture. This evidently results in a significant increase in the CO_2 content of the gaseous effluent discharged from the top of the furnace, compared to the conventional method. According to the invention, a gaseous effluent concentrated in CO_2 means that it has a CO_2 content of at least 35%, advantageously at least 45%, preferably at least 60%, 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 favourable conditions, drastically decreasing the contribution of the furnace to the greenhouse effect.

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

According to the invention, concentrated dioxygen (hereinafter referred to as oxygen), means a gas whose oxygen level exceeds 50% by volume. It will preferably be equal to or greater than 90%, in particular 93%, advantageously 98 to 100% by volume. The source of concentrated dioxygen may, for example, be an air separation unit that separates air into dioxygen and dinitrogen and works in parallel with the furnace, or a dioxygen tank installed next to the furnace. Advantageously, the fuel combustion occurs in the presence of an excess of oxygen, preferably of about 5 to 50%, in particular of 10 to 30%, advantageously of 15 to 25% by volume relative to stoichiometric combustion requirements.

According to the invention, fuel means any solid, liquid or gaseous fuel, for example natural gas, hydrogen, biogas, fuel oil, oils, coal or coke powder, solid biomass, such as sawdust, solid recovered fuel, such as plastics, paper, cardboard, etc. Advantageously, in the case of a solid fuel, the introduction thereof into the shaft in firing mode is carried out in a granular or powdered form using a portion of said collected portion of the gaseous effluent discharged from the furnace as a carrier gas. CO_2 from any other source may also be provided as a carrier gas.

According to an embodiment of the invention, cooling the calcined material comprises, at the bottom of each of the shafts, supplying cooling air which flows counter-currently through the descending calcined material and is heated on contact with it, the heated cooling air mixing with the gaseous stream containing the combustion fumes in the shaft in firing mode before moving through the gas transfer channel and, after moving, with this gaseous stream in said at least one shaft in preheating mode, the gaseous effluent concentrated in CO_2 discharged from the furnace containing the combustion fumes and the cooling air. In this case, only the combustion air of the conventional method is replaced by the oxidising mixture based on the gaseous effluent concentrated in CO_2, discharged from the furnace, and oxygen. Such a method makes it possible to increase the CO_2 content of the gaseous effluent discharged from the conventional PFRK furnace from 20 to 27% by volume on dry gas to a value of at least 35%, advantageously at least 45%, and even up to 65% by volume on dry gas in a furnace according to the invention. For illustration, a PFRK furnace using this method may advantageously replace the coke oven currently used in soda ash plants, to provide fumes with 40% CO_2 by volume. Additionally, the PFRK is a "sustainable", energy-efficient furnace, and above all it removes all environmental problems linked to coke ovens, including significant emissions of pollutants (CO, NH_3, H_2S, etc.).

According to a particular embodiment of the invention, the cooling air is supplied to the furnace in a total volume equal to or less than a thermodynamic minimum necessary to cool the calcined material to a reference temperature of 100°C. Advantageously, the total volume of cooling air supplied to the furnace may be about 40 to 60% of said thermodynamic minimum, preferably equal to 50% thereof. In this case, the unloaded product will have a higher temperature than normal operation. It is therefore necessary to adapt the unloading equipment to materials resistant to this temperature.

It may also advantageously be provided that said cooling of the calcined material comprises, at the bottom of the only shaft in firing mode, supplying cooling air which flows counter-currently through the descending calcined material and is heated on contact with it, the heated cooling air mixing with the gaseous stream containing the combustion fumes before moving through the gas transfer channel, and the gaseous effluent concentrated in CO_2 discharged from the furnace containing the combustion fumes and the cooling air. In this case too, the cooling air may be supplied to the furnace in a total volume lower than a thermodynamic minimum necessary to cool the calcined material to a reference temperature of 100°C. Advantageously, the total volume of cooling air supplied to the furnace may thus be about 40 to 60% of said thermodynamic minimum, preferably equal to 50% thereof.

According to a particularly advantageous embodiment of the invention, said cooling of the calcined material comprises, at the bottom of each of the shafts or at the bottom of the only shaft in firing mode, supplying cooling air which flows counter-currently through the descending calcined material and is heated on contact with it, the method further comprising removing the heated cooling air from the furnace, the gaseous effluent discharged from the furnace containing a CO_2 content of at least 90% by volume on dry gas, preferably at least 95%. In this case, the gaseous effluent discharged from the furnace is formed almost exclusively from combustion fumes. It becomes possible to use such a gas in specialised industries or to sequester it.

According to a particular embodiment of the invention, the method further comprises a heat exchange between the heated cooling air removed from the furnace and said collected portion of gaseous effluent discharged from the furnace, before or after it is mixed with concentrated dioxygen. This allows heat recovery in the oxidising mixture to be introduced into the shaft in firing mode.

Other details and features of the method according to the invention are mentioned in the appended claims.

Other features of the invention will also be apparent from the description below, which is non-limiting and refers to the appended drawings.

Figure 1 schematically shows a conventional PFRK furnace.

Figures 2a and 2b show a digital modelling of the oxygen mass % concentration of the gaseous streams in a conventional PFRK furnace with a circular cross-section and in a conventional PFRK furnace with a rectangular cross-section.

Figures 3 and 4 schematically show several embodiments of the furnace with a circular cross-section for the invention.

Figure 5 is a fragmented representation of an embodiment of the furnace with a rectangular cross-section for the invention.

In the figures, identical or similar parts use the same references. Conventionally, the shaft shown on the left is in firing 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 PFRK furnace shown is a vertical double-shaft furnace 1, 2, where the fuel is injected alternately in one shaft 1 then in another 2 for approximately 12 minutes with a stop period between cycles of 1 to 2 minutes to reverse the circuits. This is the “reversing” period. Both shafts have a circular cross-section and are provided with peripheral channels 13 which are interconnected by a connecting flue 3. The shafts are divided vertically into three areas, the preheating area A where the carbonate rock is preheated before calcination, the combustion area B where the firing of the carbonate rock occurs and the cooling area C where the cooling of the calcined material occurs.

When a shaft is in firing mode, here the shaft 1, a fuel supply device in the form of nozzles 4 injects a fuel 9 into the shaft, which, in the example shown, is natural gas. The carbonate rock, loaded at the top of the shaft via an inlet 5 in the open position, progressively descends in the shaft. Combustion air is introduced at the top of the shaft via a supply opening 6, which allows for fuel combustion at the outlet of the nozzles 4 and a decarbonation of the carbonate rock to calcined material 10. The gaseous stream 11 formed by the combustion and decarbonation descends co-currently to the calcined material and, using the peripheral channel 13, moves into the connecting flue 3. Cooling air is introduced via a supply duct 7 at the bottom of the shaft, counter-currently to the calcined material, to cool it. The heated cooling air 12 mixes with the gaseous stream containing the combustion fumes 11 in order to move into the connecting flue 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 nozzles 4 are therefore off. The same applies to the inlet 5 for the carbonate rock and to the opening 6 for supplying combustion air. However, the supply duct 7 for the cooling air and the outlet 8 for the calcined material remain in the open position. After heat exchange with the descending calcined material 10, the heated cooling air mixes with the gaseous stream 11 which, from the connecting flue 3, enters the shaft via the peripheral channel 13. This gaseous stream 11 progresses until it reaches the top of the shaft where it is discharged from the furnace via a discharge duct 14 and transferred to a chimney 15. In the shaft in firing mode 1, this discharge duct 14 is closed.

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

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

Figure 1 shows a furnace designed for producing 430 tonnes of lime per day. All of the gas flows mentioned in the following are expressed in Nm^3/t of lime produced.

In order to react with the gas injected as a fuel into the shaft 1, 1120 Nm^3/t of combustion air are used to obtain an excess of air of 19% by weight relative to stoichiometric requirements, and in order to form a volume of 100 Nm^3/t of CO_2 at combustion. The mass concentration of oxygen in the entering gas is 23%, since it is air. The temperature reached is then far above 900°C, causing a decarbonation of the limestone rock with a release of 380 Nm^3/t of CO_2. In order to cool the lime produced to a temperature of about 100°C, 290 Nm^3/t of cooling air are introduced via the bottom of both shafts, which makes a total of 580 Nm^3/t. At the chimney, 2250 Nm^3/t of gaseous effluent are obtained which contains 480 Nm^3/t of CO_2, i.e., this gaseous effluent has a CO_2 content of 23% on dry gas. The CO_2 is difficult to use or sequester at this low content and the gaseous effluent is therefore totally released into the atmosphere.

Figure 2a shows a digital modelling of the PFRK furnace with a circular cross-section, showing the routes of the gases according to their oxygen content. It only shows the combustion area B, from the end of the nozzles, and the cooling area C, and therefore the top of the shafts is not shown.

Areas a: in the shaft in firing mode, cooling air (at the bottom) and combustion air (at the top, just above the end of the nozzles) with an O_2 content of 23% by weight.

Areas b: combustion fume jets emitted by the nozzles, in which there is hardly any oxygen left and between which some unreacted O_2 can still be found.

Area c: the fumes penetrate deeply into the cooling area C by mixing gradually with the cooling air. They push the gaseous mixture peripherally into the peripheral channel 13, then the connecting flue 3.

Area d: in the shaft in preheating mode, cooling air.

Area e: mixture of the gaseous stream from the peripheral channel 13 and the cooling air. The closer to the centre of the shaft, the more the residual O_2 content increases.

Figure 2b shows such a digital modelling on a PFRK furnace whose shafts have a rectangular cross-section. Here, the distribution of gas flows is no longer symmetrical like it is in the case of circular shafts.

Figure 3 is a view of a furnace for the present invention. In this case, there are no changes to the structure of the furnace. A separating member 17, capable of collecting a portion of gaseous effluent discharged from the furnace and introducing it into the recirculation circuit 18 has been provided on the exterior, on the discharge duct 14. In this circuit, the collected portion of gaseous effluent is advantageously treated in a treatment unit 19, where it may, for example, be filtered and/or dried. An air separation unit 20 separates air supplied by the duct 21 into 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 oxidising mixture formed from the recirculated portion of gaseous effluent and concentrated O_2 to the top of each of the shafts at the supply opening 6.

The operation of the furnace in Figure 3 is similar to a PFRK furnace. The separating member 17 is continuously in service, the same as the treatment unit 19 and the air separation unit 20. As has already been seen, the reversing system 16 closes the discharge duct 14 at the top of the shaft in firing mode. However, at the top of this shaft, it opens the supply opening 6 to allow the oxidising mixture to be introduced, while it is closed at the top of the shaft in preheating mode.

The same amount of carbonate rock and the same flows of fuel and cooling air are used as in the conventional furnace described above. 830 Nm^3/t of gaseous effluent discharged from the furnace, rich in CO_2, is collected via the recirculation duct 18. This recirculated effluent is mixed with 160 Nm^3/t of O_2, to maintain the same mass concentration of 23% of O_2 in the oxidising mixture thus formed and to obtain the same excess of oxygen of 19% by weight relative to stoichiometric requirements during combustion. The nitrogen N_2 of the combustion air is thus replaced by the mass equivalent thereof of CO_2. Since this is heavier than dinitrogen (specific weight of 1.977 relative to 1.25 g/Nm^3), the total volume of the fumes decreases in the furnace, which causes a decrease in the pressure drop of 13% relative to the conventional furnace. At the chimney, 1240 Nm^3/t of gaseous effluent is released which, at present, contains 43% by volume on dry gas of CO_2. As explained above, industrial use becomes possible at this content, for example in soda ash plants.

As a variant in such a furnace for the invention, in order to further decrease the input of air in the method, the flow of cooling air may be reduced. For example, this input may be reduced to 50%, which is 290 Nm^3/t of cooling air. This reduced volume may be introduced via the supply duct 7 of the only shaft in firing mode or by making use of the supply ducts 7 of both shafts. This measurement reduces the dilution of the fumes by 50%. This results in less cooling of the calcined material that is discharged via the outlets 8. Thus, it becomes necessary to provide unloading equipment that is resistant to a temperature higher than 100°C, for example, a refractory steel unloading table and steel drag chains. Since the lime exits hotter, there has been less heat recovery by the cooling air, which is compensated by a small increase in the input of fuel to a flow such that it causes 120 Nm^3/t of CO_2 to be formed at combustion. In turn, this increase requires changing the collection of 1730 Nm^3/t of gaseous effluent discharged from the furnace in the recirculation circuit to 865 Nm^3/t and mixing this collected effluent with 200 Nm^3/t of O_2 so as to maintain the same mass concentration of 23% of O_2 in the oxidising mixture thus formed and to obtain the same excess of oxygen of 19% by weight relative to stoichiometric requirements during combustion. At the chimney, only 865 Nm^3/t of gaseous effluent with a high CO_2 content of 63% by volume on dry gas is thus obtained.

In fact, a custom CO_2 concentration between 40% and 65% by volume of CO_2 can be established at the chimney by adjusting the amount of cooling air to between 100% and 50% of the thermodynamic minimum volume necessary to cool the calcined material to a reference temperature of 100°C. A higher concentration of CO_2 may be able to be obtained by reducing the input of cooling air to below 50%, within the temperature compatibility limit of the lime with the high-temperature unloading and transport system installed for this purpose.

Figure 4 is a view of an advantageous furnace for the present invention. As can be seen, this furnace comprises the features of Figure 3, but, in addition, comprises a small transformation of the external structure of the furnace.

In this case, the heated cooling air is extracted by contact with the calcined material, by installing a removal system. The shafts 1 and 2 are each provided with a collector ring 25, below the connecting flue 3 and the peripheral channels 13, which connects with an evacuation element 26 so as to allow heated cooling air to be removed from the furnace. In this way, a portion or all of the combustion air may be extracted, as required, by also extracting a small proportion of combustion fumes. Indeed, as Figure 2a shows, because the descending gases penetrate deeply into the cooling area C, the cooling air is pushed towards the external walls of the furnace where the collector ring is arranged. The shafts may further optionally comprise, at the bottom, a central collector element 27 connecting with the evacuation element 26 as to also allow a central removal of the heated cooling air, below the connecting flue 3.

In the case of rectangular furnaces, it is also possible to extract the cooling air without a collector ring, using side recovery areas. As can be seen in Figure 5, each shaft includes 4 sides. A side 28 of one shaft faces a side 29 of the neighbouring shaft and each shaft includes a second side 30 and 31, respectively, which is opposite to those facing each other. The gas transfer channel is a connecting flue 3 which directly connects one shaft to the other via the sides 28 and 29 thereof. Below the connecting flue, the sides 28 to 31 are each provided with a collection tunnel 32 to 35, respectively, connecting with an evacuation element 26 so as to allow heated cooling air to be removed from the furnace.

Since the spread of gaseous streams in a rectangular-shaft furnace is not symmetrical (see Figure 2b), the cooling air is only pushed by the hot fumes to one side. Also, in the furnace shown where the shaft 1 is in firing mode and the shaft 2 in preheating mode, the reversing system 16 only opens the collection tunnels 32 and 34. During the following cycle, only the collection tunnels 33 and 35 will be open.

In the furnace shown in Figure 4, the same amount of carbonate rock and the same flows of cooling air are used as in the conventional furnace described above. The heated cooling air is removed from the furnace via the evacuation element 26. In the shaft 1, a fuel introduction is performed such that the formation of 105 Nm^3/t of CO_2 is obtained at combustion. At the top of the shaft 2, 1330 Nm^3/t of gaseous effluent is discharged. 730 Nm^3/t of this discharged gaseous effluent rich in CO_2 is collected via the recirculation circuit 18. This recirculated effluent is mixed with 220 Nm^3/t of O_2 so as to maintain the same mass concentration of 23% of O_2 in the oxidising mixture thus formed and to obtain the same excess of oxygen of 19% by weight relative to stoichiometric requirements during combustion. At the chimney, only 600 Nm^3/t of gaseous effluent with a content of 96% on dry gas of CO_2 is thus obtained.

In the furnace shown in Figure 4, in order to recover a portion of the energy from the hot air removed by the evacuation element 26, a heat exchange may be provided with the portion of recirculated gaseous effluent using a heat exchanger 36, before or after the mixing thereof with concentrated dioxygen.

Furthermore, in the connecting flue 3 and the peripheral channels 13, an injection of a fraction of said collected portion of gaseous effluent discharged from the furnace using an injection duct 37 may also be provided. Optionally beforehand, a heat exchange between the heated cooling air removed from the furnace, and this above-mentioned fraction to be injected may occur using a heat exchanger, for example the heat exchanger 36. In the absence thereof, a heat exchanger not shown may be provided on the injection duct 37.

According to yet another variant, the temperature in the connecting flue may be mitigated by injecting water at selected locations of the flue and/or peripheral ring. This added water has no dilution effect on the concentration of CO_2 on dry gas.

Such arrangements to recover the heat from the heated cooling air removed from the furnace, using a heat exchanger as well as such CO_2 or water injecting devices in the connecting flue may also naturally be provided with rectangular-shaft furnaces.

It is clear that a furnace similar to that shown in Figure 4 may be designed, where the cooling air is injected at the bottom of only one of the two shafts.

Table 1 below includes the flows in a conventional furnace and in different furnace variants for the invention and Table 2 includes the amounts of the various gaseous elements at the inlet of the furnaces.

In the examples column, 1 indicates a conventional PFRK furnace, 2 and 3 are furnaces according to Figure 3 with variable flows of cooling air and 4 and 5 are furnaces according to Figure 4 with and without a heat exchanger.

Table 1

	Combustion air Nm³/t	Cooling air Nm³/t	O_2 injection Nm³/t	Recycled effluent Nm³/t	Effluent at the top of the furnace Nm³/t	Chimney effluent Nm³/t	DP*
1	1120	580	0	-	2250	2250	DP_0
2	0	580	160	830	2070	1240	-13%
3	0	290	200	865	1730	865	-26%
4	0	580	220	730	1330	600	-49%
5	0	580	250	820	1440	620	-39%

*DP = pressure loss

Table 2

	O_2 injection Nm³/t	O_2 kg/t	N_2 kg/t	CO_2 kg/t	Mass % of O_2	Stoichiometric O_2 kg/t	Excess of O_2 %
1	0	333	1090	0.89	23	281	19
2	160	331	448	646	23	278	19
3	200	367	277	915	23	303	18
4	220	346	5	1143	23	294	18
5	250	394	6	1284	23	327	20

It is understood that the present invention is in no way limited to the embodiments described above and that changes can be made without departing from the scope of the appended claims.

For example, replacing the fuel injection nozzles, cooled by air, with thermally insulated nozzles may be advantageously provided.

PATENTTIVAATIMUKSET

1. Menetelmä mineraalikiven kalsinoimiseksi regeneratiivisessa, samansuuntaisiin virtoihin perustuvassa pystykuilu-uunissa, jossa vähintään kaksi kuilua on liitetty yhteen kaasunsiirtokanavalla, tässä menetelmässä, tuotannon aikana,

- syötetään karbonaattinen mineraalikivi uunin yläosaan,
- esilämmitetään tämä kivi,
- poltetaan tämä kivi, jolloin sen dekarbonointi tuottaa kalsinoitua ainesta,
- jäähdytetään kalsinoitu aines jäähdytysilmalla, ja
- poistetaan kalsinoitu aines kuilujen pohjasta,
- jokaisen kuilun toimiessa vuorotellen polttotilassa ja esilämmitystilassa, yhden kuilun ollessa polttotilassa ennalta määritetyn ajanjakson ajan samalla kun vähintään yksi toinen kuilu on esilämmitystilassa, ja päinvastoin,
- jossa polttotilassa:

  suoritetaan mainittu karbonaattisen mineraalikiven syöttö polttotilassa olevan kuilun yläosaan,
  mainitun karbonaattisen mineraalikiven läsnäollessa, sen siirtyessä esilämmitettynä alaspäin tässä kuilussa, sytytetään polttoaine palamaan hapen läsnäollessa siten, että aikaansaadaan tämän kiven mainittu poltto ja sen dekarbonointi kalsinoiduksi ainekseksi, jolloin samalla vapautuu kaasuvirran muodossa olevia palamiskaasuja, jotka laskeutuvat yhteisvirtana alaspäin polttotilassa olevassa kuilussa, ja
  annetaan näitä palamiskaasuja sisältävän mainitun kaasuvirran siirtyä polttotilassa olevasta kuilusta mainittua vähintään yhtä esilämmitystilassa olevaa kuilua kohti mainitun kaasunsiirtokanavan välityksellä,
- jossa esilämmitystilassa:

  suoritetaan mainittu syötetyn karbonaattisen mineraalikiven esilämmitys lämmönvaihdolla kaasunsiirtokanavasta peräisin olevia palamiskaasuja sisältävän kaasuvirran kanssa, kaasuvirran noustessa ylöspäin mainitussa vähintään yhdessä esilämmitystilassa olevassa kuilussa, ollen näin vastavirrassa mainitun syötetyn karbonaattisen mineraalikiven suhteen, ja poistetaan palamiskaasuja sisältävään kaasuvirtaan perustuvat kaasupäästöt uunista mainitun vähintään yhden esilämmitystilassa olevan kuilun yläosasta,

tunnettu siitä, että mainittu polttoaineen sytyttäminen tapahtuu siten, että happea on läsnä ylimäärin stökiometristen tarpeiden suhteen, ja siitä, että menetelmässä lisäksi:

- otetaan talteen osa uunista poistetuista kaasupäästöistä,
- muodostetaan hapettava seos sekoittamalla tämä uunista poistetuista kaasupäästöistä talteenotettu osa konsentroidun hapen kanssa, ja
- syötetään tämä hapettava seos polttotilassa olevan kuilun yläosaan siten, että varmistetaan mainittu polttoaineen syttyminen palamaan hapen läsnäollessa,

uunista poistettujen kaasupäästöjen ollessa konsentroitu CO_2:n suhteen.

2. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että mainitussa kalsinoidun aineksen jäähdyttämisessä jokaisen kuilun pohjaan syötetään jäähdytysilmaa, joka kulkee vastavirtaan kalsinoidun, alaspäin siirtyvän aineksen lävitse ja joka lämpenee sen kanssa tapahtuvan kontaktin myötä, siitä, että lämmennyt jäähdytysilma sekoittuu, polttotilassa olevassa kuilussa, palamiskaasuja sisältävään kaasuvirtaan ennen kuin se siirtyy kaasunsiirtokanavan läpi ja tämän kanavan jälkeen tähän kaasuvirtaan mainitussa vähintään yhdessä esilämmitystilassa olevassa kuilussa, ja siitä, että uunista poistetut, CO_2:lla konsentroidut kaasupäästöt sisältävät palamiskaasuja sekä jäähdytysilmaa.

3. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että mainitussa kalsinoidun aineksen jäähdyttämisessä ainoan polttotilassa olevan kuilun pohjaan syötetään jäähdytysilmaa, joka kulkee vastavirtaan kalsinoidun,

alaspäin siirtyvän aineksen lävitse ja joka lämpenee sen kanssa tapahtuvan kontaktin myötä, siitä, että lämmennyt jäähdytysilma sekoittuu palamiskaasuja sisältävään kaasuvirtaan ennen kuin se siirtyy kaasunsiirtokanavan läpi, ja siitä, että uunista poistetut, CO_2:lla konsentroidut kaasupäästöt sisältävät palamiskaasuja sekä jäähdytysilmaa.

4. Patenttivaatimuksen 2 tai 3 mukainen menetelmä, tunnettu siitä, että jäähdytysilmaa syötetään uuniin siten, että sen kokonaistilavuus on yhtä suuri tai pienempi kuin termodynaaminen minimi, joka tarvitaan jäähdyttämään kalsinoitu aines 100 °C:n vertailulämpötilaan.

5. Patenttivaatimuksen 4 mukainen menetelmä, tunnettu siitä, että uuniin syötetyn jäähdytysilman kokonaistilavuus on noin 40 - 60 % mainitusta termodynaamisesta minimistä, edullisesti 50 % siitä.

6. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että mainitussa kalsinoidun aineksen jäähdyttämisessä jokaisen polttotilassa olevan kuilun pohjaan tai ainoan polttotilassa olevan kuilun pohjaan syötetään jäähdytysilmaa, joka kulkee vastavirtaan kalsinoidun, alaspäin siirtyvän aineksen lävitse ja joka lämpenee sen kanssa tapahtuvan kontaktin myötä, siitä, että menetelmässä lisäksi poistetaan lämmennyt jäähdytysilma uunista, ja siitä, että uunista poistettujen kaasupäästöjen CO_2-pitoisuus on vähintään 90 til-% kuivan kaasun suhteen.

7. Patenttivaatimuksen 6 mukainen menetelmä, tunnettu siitä, että menetelmässä suoritetaan lisäksi lämmönvaihto uunista poistetun lämmenneen jäähdytysilman sekä mainitun uunista poistetuista kaasupäästöistä talteenotetun osan välillä, joko ennen sen sekoittamista konsentroidun hapen kanssa tai tämän jälkeen.

8. Patenttivaatimuksen 6 tai 7 mukainen menetelmä, tunnettu siitä, että menetelmässä lisäksi injektoidaan mainitun uunista poistetuista kaasupäästöistä talteenotetun osan fraktio kaasunsiirtokanavaan ja valinnaisesti, ennen tätä injektointia, suoritetaan lämmönvaihto uunista poistetun lämmenneen jäähdytysilman ja edellä mainitun injektoitavan fraktion välillä.

9. Jonkin patenttivaatimuksista 1 – 8 mukainen menetelmä, tunnettu siitä, että menetelmässä lisäksi injektoidaan vettä kaasunsiirtokanavaan.

10. Jonkin patenttivaatimuksista 1 – 9 mukainen menetelmä, tunnettu siitä, että mainitussa polttoaineen sytyttämisessä syötetään polttotilassa olevaan kuiluun kaasumaista, nestemäistä tai kiinteää polttoainetta, ja siitä, että, kiinteän polttoaineen tapauksessa, mainittu syöttö suoritetaan käyttämällä osaa mainitusta uunista poistetuista kaasupäästöistä talteenotetusta osasta tai muuta CO_2-lähdettä kantajakaasuna.

Fig. 1

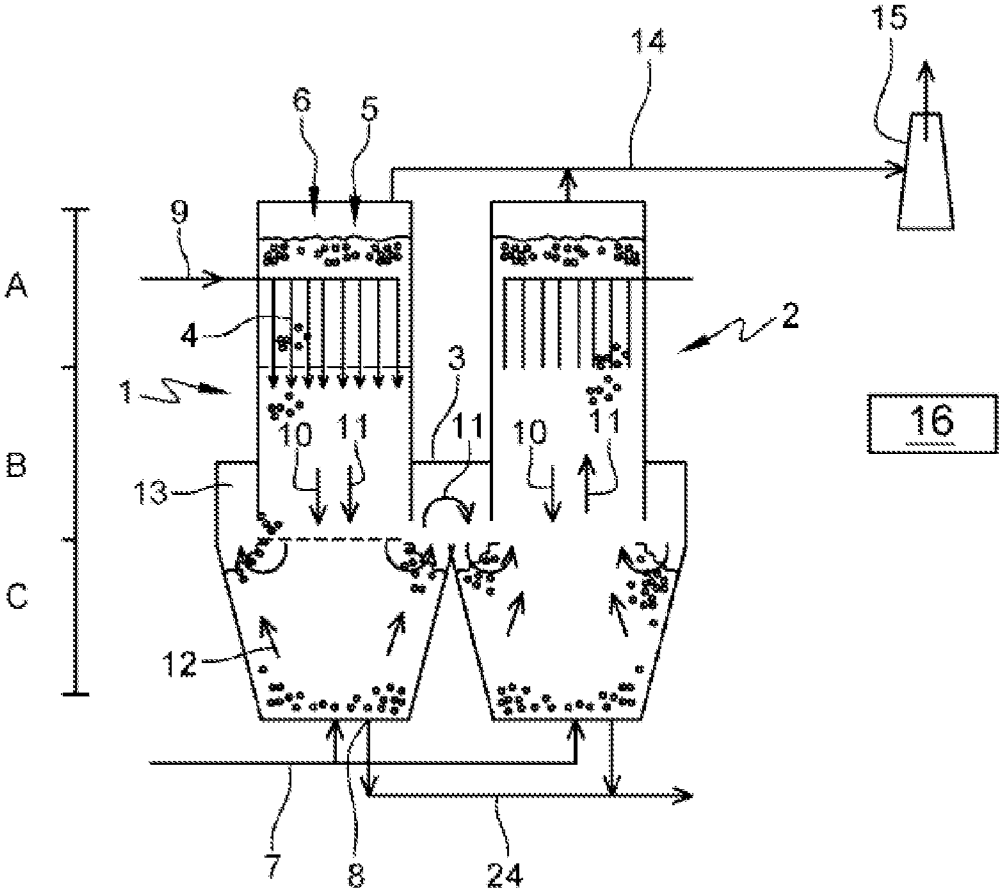

Fig. 2a

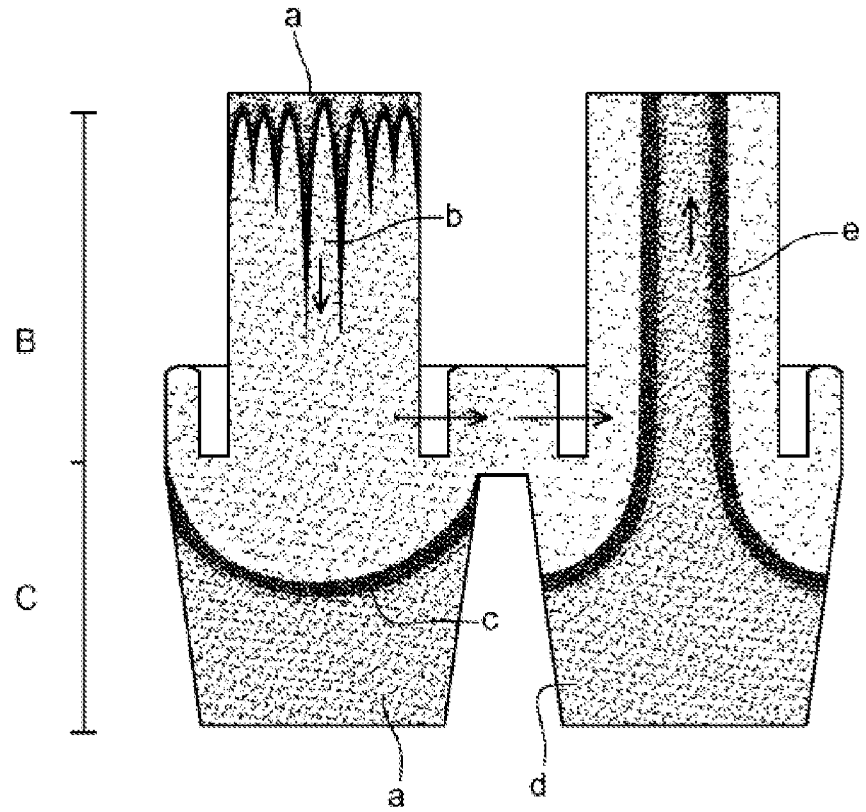

Fig. 2b

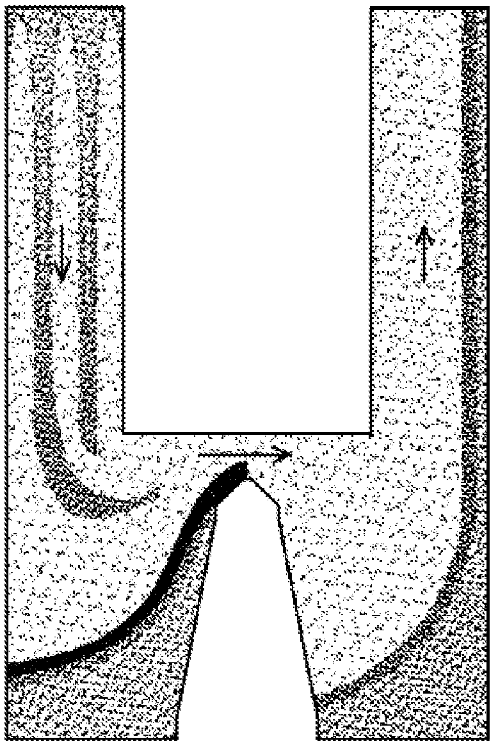

Fig. 3

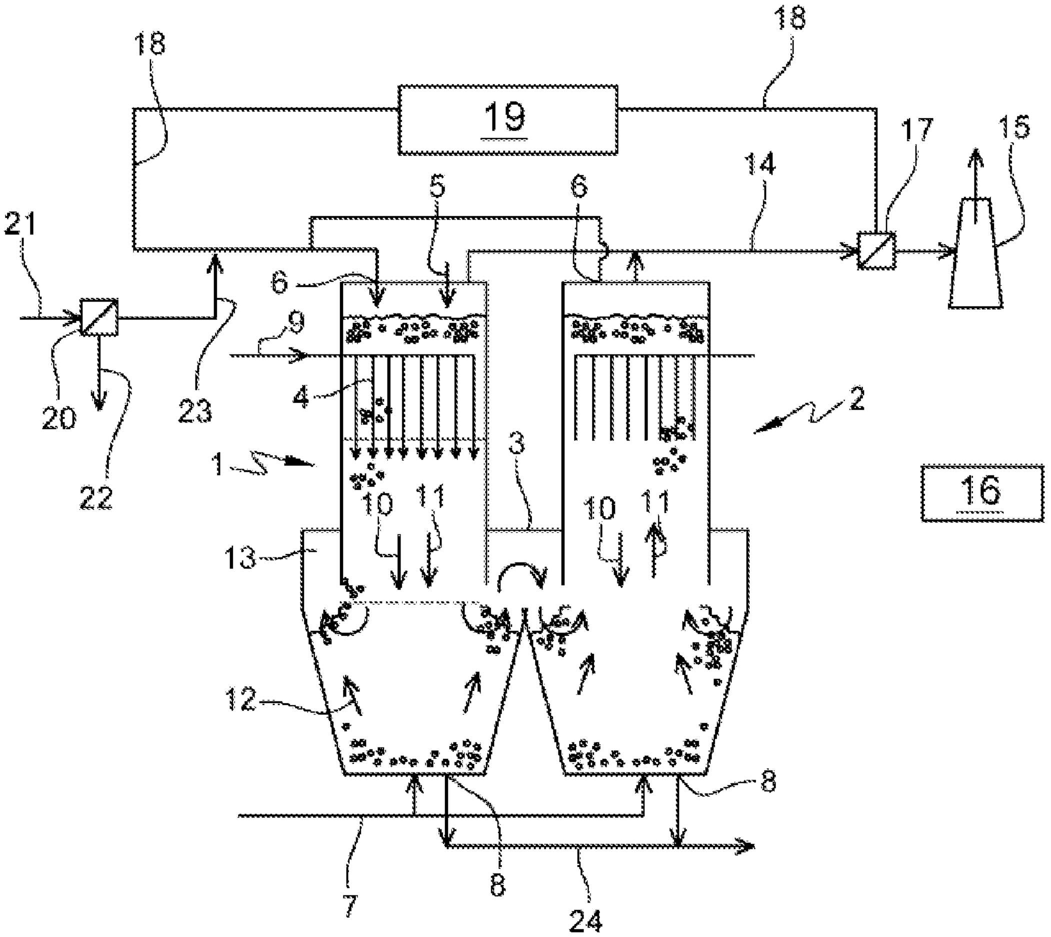

Fig. 4

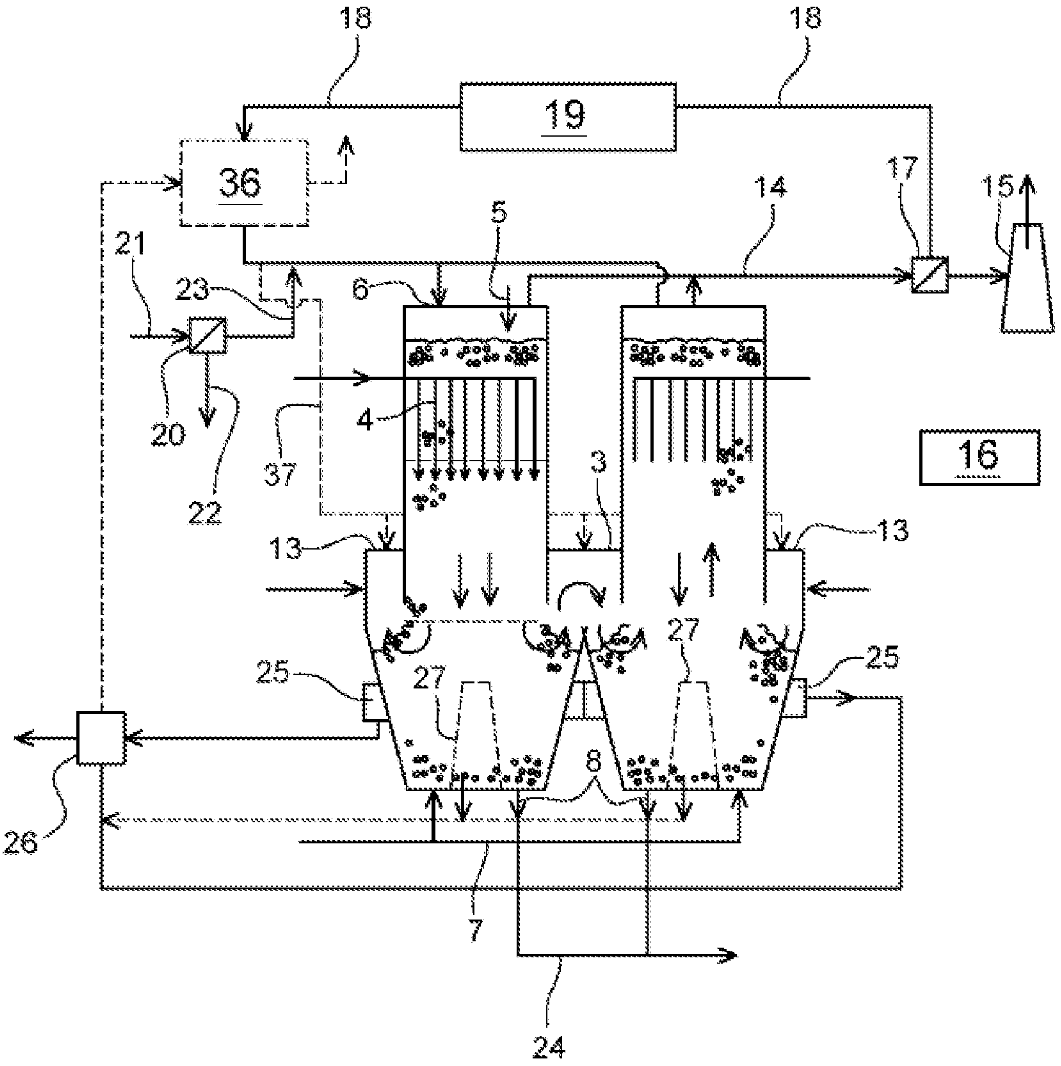

Fig. 5