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(54) Benævnelse: **Cementklinkerlinie og fremgangsmåde til drift af en cementklinkerlinie**

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DESCRIPTION

Field of the invention

[0001] The invention relates to a method for manufacturing cement clinker by sintering raw meal in a kiln to cement clinker, briefly referred to as clinker. To this end raw meal is preheated in a preheater using a main flue gas stream from the kiln as heat source. Downstream of the preheater, the flue gas is cooled to a temperature below the boiling point of mercury and dedusted, thereby obtaining mercury loaded dust. The invention as well relates to a corresponding cement clinker line.

Description of the related art

[0002] Cement clinker is an important intermediate product for concrete. Cement clinker, subsequently briefly 'clinker' is produced by calcining and sintering so called raw meal in a kiln. The raw meal is a mixture of mainly limestone and clay and/or other alumino-silicate materials. These mining products are in a first step dried using waste heat transported by kiln exhaust gas and milled. Subsequently, the such obtained raw meal is preheated in a so called preheating tower, again using kiln exhaust gas as heat source. Often, the preheated raw meal is provided to a calciner for (pre-) calcining the raw meal. The preheated and optionally (pre-) calcined raw meal is subsequently sintered in a kiln and discharged to a clinker cooler. The process is well known and an illustrative introduction is provided by Dr. Harder "Der Herstellungsprozess", published in ZKG-Handbuch Zementanlagenbau 2013/2014, p. 20 to 37, Bauverlag BV, Gütersloh.

[0003] The energy consumption of cement clinker lines is remarkable: The theoretical thermal energy for the chemical reactions in clinker manufacturing is 1.8GJ/t. Including losses 3.3GJ/t have been reported (Numbers taken from Cement chemistry, H.F.W. Taylor, table 3.3, 2nd ed.,Thomas Telford Publishing, London, 1997). Bayer reports a mean thermal energy of 2.9GJ/t of clinker for German plants in 2012 (ZKG-Handbuch Zementanlagenbau 2013/2014, p. 41). To reduce manufacturing costs, fuels like coal, gas and the like are substituted by plastic waste and other organic matter. These substitute fuels further augment the amount of heavy metals like mercury in the process that are as well introduced by the mining products. The emission of mercury has been limited by the Minamata-Convention on mercury in 2013 and thus emission limits are reduced.

[0004] The mercury vaporizes depending on its origin in the preheater and in the kiln. The same holds true for other heavy metals, dependent on their respective boiling temperatures. The gaseous mercury becomes part of the flue gas being transported towards the exhaust. However, emission of mercury via the exhaust has a negative impact on the environment and should be avoided. A further part of the mercury condenses on or is adsorbed by the dust being transported by the flue gas and is separated from the flue gas. However, the dust is usually reintroduced to the process (typically via the preheater) as it main constituents are clinker dust and raw-meal dust. Thus, when heating the dust in the preheater, the mercury evaporates again and when cooling the flue gas down, the mercury condenses again on the dust. Accordingly, the mercury concentrates in the manufacturing line.

[0005] The authors of US 2015/0086453 suggest to inject metal sulfide compounds or organic sulfide compounds into the kiln to thereby decompose the compounds and release elementary sulfur. This elementary sulfur reacts with elementary mercury to mercury sulfides. Mercury sulfide can be captured using bag filters or electrostatic precipitators.

[0006] In WO 2010/107404 it is suggested to dedust the still hot flue gas downstream the preheater using an electrostatic precipitator. The dedusted flue gas is subjected to a selective catalytic denitrification and cooled down to about 125°C by injecting water. Subsequently, an adsorbent is injected to the cooled flue gas stream. The mercury attaches to the adsorbent and is removed from the flue gas by a downstream bag filter prior to releasing the flue gas via an exhaust.

[0007] US 2010/041690 A1 suggest to reduce mercury emissions of a cement clinker line, by removing mercury from a chloride bypass stream. In a first step the chloride bypass stream is cooled below the condensation temperature of alka-li chlorides, which in turn condense on the kiln dust. The mercury remains in the gas phase of the bypass gas stream. The dust is removed by a first hot gas dust collector and subsequently, mercury containing particulate material is brought in direct contact with the previously dedusted bypass gas stream in a reactor. Accordingly, the particulate matter heats up and the mercury enters the gas phase. The particulate material is thus cleaned from mercury and thus removed from the bypass gas stream by a second hot gas dust collector. The cleaned particulate matter is subsequently fed to the kiln. The bypass gas stream is now cooled down and an adsorbent is injected into the stream, to thereby attach the mercury to the adsorbent. Removal of the adsorbent from the bypass stream by a third dust collector removes the mercury from the clinker line.

[0008] DE 10 2011 052 561 A1 suggests to use excess heat of bypass gas stream of a cement clinker line as heat source of a steam boiler. As usual, the bypass gas stream is withdrawn from the kiln exhaust and cooled down below the condensation temperature of the alkali chlorides by adding fresh air to the bypass gas stream. The alkali chlorides thus condense on the dust and can be re-moved from the clinker line by dedusting the bypass gas stream. After dust removal, the bypass gas stream is provided to the steam boiler.

Summary of the invention

[0009] The problem to be solved by the invention is to reduce mercury emissions and in at least in part other heavy metal emissions of a cement clinker line at reduced operating costs.

[0010] Solutions of the problem are described in the independent claims. The dependent claims relate to further improvements of the invention.

[0011] The invention is based on the observation, that heavy metal emission, like e.g. mercury emissions are low during ramp up. It thus appears that the mercury has to accumulate in the cement clinker line before it leaves the process via the exhaust. According to the invention, it is thus sufficient to maintain a low mercury concentration in the cement clinker line to reduce mercury emissions via the exhaust gas. This applies accordingly to other heavy metal emissions.

[0012] The method for manufacturing clinker comprises at least sintering raw meal in a kiln to clinker. As usual the raw meal is preheated in a raw meal preheater, briefly 'preheater' using the flue gas produced in the kiln. After preheating, the raw meal is provided to the kiln for calcining and sintering the raw meal to clinker. Of course, the method may as well comprise calcining the preheated raw meal at least partially in a calciner and thus a part of the flue gas may be produced in the calciner, but this is well known and thus not focused here. Only for simplicity the invention is explained without explicit reference to an optional calciner. Thus, the term kiln may be understood to optionally include a calciner. In any case the preheated raw meal is fed to the kiln for converting it into clinker.

[0013] The flue gas exiting the preheater is processed as usual and thereby further cooled down to a temperature where mercury and/or mercury compounds condense on the dust particles being transported by the main flue gas stream. Similarly, other heavy metals and their compounds condense on the dust particles.

[0014] The cooled main flue gas stream is dedusted by main flue gas dedusting means downstream of the preheater, for example using at least one bag filter or hose filter. This dedusting thus provides a mercury loaded dust. Other heavy metals and/or heavy metals compounds are as well attached to the dust. Below, we simply refer to the term 'mercury loaded dust', without explicit reference to other heavy metals and heavy metal compounds. The mercury loaded dust consists mainly of clinker dust and raw meal, but mercury and other heavy metals which have been transported with the main flue gas stream are adsorbed by the dust particles when cooling the main flue gas stream down. This adsorption is enhanced if the main flue gas stream is cooled below the boiling temperature of mercury or the respective mercury compounds, e.g. mercury halogenides. Preferably, the main flue gas stream is cooled down to about 250°C or lower, thereby enabling dedusting the flue gas using bag filters, which have lower installation costs than electrostatic precipitators or ceramic filters. Beyond, the lower the temperature of the flue gas (prior to dedusting) the better the mercury attaches to the dust and thus the lower is the mercury content in the dedusted main flue gas stream.

[0015] Cooling of the main flue gas stream can be obtained, e.g. by using a heat exchanger which in turn heats another fluid (or raw meal); thus the thermal energy transported with the flue gas can be used as process heat, e.g. for a turbine process. Other possibilities of cooling can be used as well, e.g. mixing the main flue gas stream with a cold(er) gas, by water spray cooling and the like. The flue gas may as well be denitrified, for example as explained in EP 2 545 337. For the invention it is not relevant at which particular stage of the process dedusting of the main flue gas takes place (e.g. prior or after denitrification), but at least one dedusting step should take place at a temperature level where a significant part of the mercury content in the flue gas is attached to or otherwise adsorbed by the dust particles. The dust is thus mercury loaded and its main constituents are raw meal and clinker fines.

[0016] At least a fraction of the mercury (and other heavy metals) of the mercury loaded dust is vaporized in a flue gas stream. Different form the theoretic definition of 'vaporizing', vaporization of mercury here simply means to subject it to a phase transition from solid or fluid to a gaseous state no matter how this phase transition takes places in detail. In other words, after the vaporization, the mercury is at least to a large extent in a gaseous state no matter which particular process is used (e.g. sublimation, vaporization, evaporation, boiling...). One could as well use the term 'gasification', but this term is typically used only for converting hydrocarbon fuels to carbon monoxide and could thus be potentially misleading.

[0017] Vaporization of the mercury (and other heavy metals) can be obtained, by injecting at least a fraction of the mercury loaded dust into to an auxiliary flue gas stream, which is provided by branching of a fraction of the main flue gas stream originating from the kiln. The remaining (main) fraction of the main flue gas stream (subsequently briefly main flue gas stream) is processed as usual and explained above. This auxiliary flue gas stream is preferably branched off, i.e. drawn off, from the main flue gas stream downstream the preheater, but prior to cooling the main flue gas stream below the boiling point of mercury, e.g. by the above mentioned cooling step. Alternatively the auxiliary flue gas stream may e.g. be drawn off from an intermediate gas exit of the preheater. The intermediate exit may, e.g. enable to draw off auxiliary gas between two cyclones of the preheater.

[0018] Alternatively, the mercury can be vaporized using the heat of the main flue gas stream, by injecting at least a fraction of the mercury loaded dust into the main flue gas stream upstream of the branch for drawing off the auxiliary flue gas stream. For example, said fraction of the mercury loaded dust can simply be added to the preheater. In the preheater, the mercury heats up, becomes gaseous and leaves the preheater with the main flue gas stream. The 'de-mercurized' dust enters the kiln (at least mainly) and is processed to clinker.

[0019] Only to avoid ambiguities, injecting a fraction of mercury loaded dust or matter to a gas stream simply means to add the fraction of dust to the respective gas stream. In other words, the fraction is disposed in the corresponding duct, e.g. using a mixing chamber, a rotary feeder and/or the like. After injecting, the mercury loaded raw meal may be transported with said respective gas stream. For example, the dust is thereby heated by the auxiliary flue gas stream, and due to the heating the mercury changes into its gaseous state.

[0020] The auxiliary flue gas stream is preferably a fraction (typically 1% to 10% or higher) of the main flue gases stream, which is separated from the main flue gas stream. As indicated above, the auxiliary flue gas stream may for example be drawn off from the preheater, e.g.

after the last cyclone. Measurements revealed a remarkable mercury concentration in the main flue gas stream in the preheater already prior to the last cyclone ('last' cyclone refers here to direction of the flow of the flue gas). Thus, a mercury loaded flue gas fraction, providing said auxiliary flue gas stream can be drawn off between the preheater stages. Drawing off the auxiliary flue gas stream prior to the last stage of the preheater provides an accordingly hotter auxiliary flue gas stream. In turn the flow rate of auxiliary flue gas being required to heat a given amount (per unit of time) of mercury loaded dust above the vaporization temperature of mercury or the relevant mercury compounds can be reduced, thereby reducing installation costs. Further, due to the higher temperatures other heavy metals with higher boiling temperatures can be vaporized from the dust as well and thus separated from the dust.

[0021] After vaporizing the mercury (or other heavy metals) comprised in the mercury loaded dust by the heat provided by the auxiliary flue gas stream (as well briefly 'auxiliary gas' or 'auxiliary flue gas' or 'auxiliary gas stream') or the main flue gas stream, the auxiliary flue gas stream is dedusted in a first auxiliary flue gas dedusting step. The temperature of the auxiliary flue gas stream in the dedusting step should preferably be selected to be at least slightly above the boiling temperature of mercury (or the respective mercury compounds) to prevent condensation of mercury on the dust. It can be even below the boiling point, as elementary mercury has a significant vapor pressure even at temperatures below its boiling point. In the latter case, a part of the mercury will be removed with the dust (this is possible, but not intended). The object of the temperature setting is to obtain at least essentially mercury free dust. The mercury free dust may be provided to the kiln for converting it into clinker, e.g. via the preheater. The term mercury free dust should thus be understood as dust with a (significantly) reduced mercury content compared to the mercury content prior to heating the mercury loaded dust.

[0022] The mercury is thus still in the auxiliary flue gas stream and is bound to an adsorbent. To this end the auxiliary gas stream is cooled down to a temperature preferably well below the boiling temperature of mercury, e.g. 70 to 150°C after the first dedusting step. Cooling may be obtained using a heat exchanger, like for example a steam boiler, to enable using the heat transported by the auxiliary flue gas stream as process heat. In addition, e.g. after or prior this cooling step of the auxiliary gas stream, an adsorbent may be injected into the auxiliary flue gas stream. The mercury and other heavy metals attach to the adsorbent and can be removed from the auxiliary gas stream with the adsorbent by simple filtering or other dedusting techniques. More generally, the auxiliary gas stream is dedusted (again) by adsorbent removal means to remove the mercury loaded adsorbent from the auxiliary gas stream. The adsorbent may comprise or even consist of activated charcoal particles. Other particles can be used as well or in addition, e.g. clinker dust and / or raw meal as initially injected into the auxiliary flue gas stream. At least a fraction of the removed mercury loaded adsorbent is preferably removed from the process and replaced by fresh adsorbent. Another fraction of the removed adsorbent can be reinjected to the preferably cooled auxiliary gas stream upstream of the adsorbent removal means, i.e. it is recircled and only a fraction is preferably replaced by fresh adsorbent.

[0023] The above outlined scheme enables to essentially remove the mercury (and other heavy metals), which is (are) added to the process by the mining products and the fuel from the process and thus to keep mercury emissions via the exhaust low.

[0024] The auxiliary gas is subjected to a denitrification prior to the second cooling step. A reductant is injected prior to the first auxiliary gas dedusting step and the dedusting means comprise or consists of a filter comprising a catalyst for denitrification, i.e. for converting nitrogen oxides to harmless substances like diatomic nitrogen and water. Such filters may comprise ceramic filter elements into which at least one catalyst is embedded or incorporated. In other words, the filter comprises at least one catalytic substance like titanium oxide, oxides of base metals (such as vanadium, molybdenum and tungsten), zeolites and/or precious metals. These catalysts not only reduce the nitrogen oxides, but as well convert elementary mercury (Hg) to a higher oxidation state, e.g. to Hg^{+2}. This oxidized mercury forms compounds like mercury chloride or mercury bromide which attach better to the adsorbent due to their lower boiling point and the lower vapor pressure below their respective boiling points. Subsequent mercury removal is thus enhanced by the catalyst. In addition the catalyst removes dioxins and other volatile organic substances that would as well attach to the adsorbent, at least if the adsorbent is activated charcoal. Thus, the active surface of the adsorbent is not reduced by organic substances.

[0025] A similar effect can be obtained, if the SCR-process and dedusting are separated, i.e. the auxiliary flue gas can be dedusted (e.g. using an electrostatic precipitator) and subsequently provided to a catalyst for denitrification. The reductant is injected to auxiliary flue gas stream upstream of the catalyst.

[0026] At least a fraction of the mercury loaded dust may be added to a flow of transport gas, conveying the mercury loaded dust to the respective flue gas stream to which it is injected. By mixing the transport gas with the main flue gas stream and or the auxiliary flue gas stream (e.g. in one or more mixing chambers), the mercury loaded dust may be injected into the respective flue gas flow.

[0027] Preferably, the transport gas is branched off from the main flue gas flow after cooling it below the mercury boiling temperature, preferably prior to dedusting it for obtaining the mercury loaded dust. At least a fraction of the mercury loaded dust provided by the flue gas dedusting means may be added to the transport gas flow and mixed with the auxiliary gas as cooling gas to thereby inject the mercury loaded dust into the auxiliary gas and thus vaporize the mercury. Thereby, no oxygen is added to the auxiliary flue gas stream and the transport gas is available at the place where the mercury loaded dust is provided. Accordingly, installation costs can be kept low. The dust is removed as explained above and can be added to the clinker as it is essentially free of mercury.

[0028] Preferably, the dedusted auxiliary gas stream is provided to a heat exchanger for heating a heat carrier fluid and in turn cooling the previously dedusted auxiliary gas stream down to a temperature below the boiling temperature of mercury. Thus, the mercury can be adsorbed effectively by the adsorbent and the thermal energy being transported by the auxiliary gas stream can be recuperated and used a process heat.

[0029] As explained above, a fraction of the removed adsorbent may be injected into the cooled auxiliary flue gas stream again and another fraction may be removed from the process. This enables to efficiently use the adsorbent and keep the amount of adsorbent to be deposited due to its mercury load low.

[0030] As already apparent from the above, the main flue gas stream is preferably cooled after the preheater and prior to its dedusting. There may be an additional dedusting step prior to cooling the main flue gas flow below the boiling point of mercury, to thereby remove a part of the dust prior to condensing the mercury on the remaining dust. Thereby, the amount of mercury loaded dust is reduced and the mercury concentration of the mercury loaded dust is enhanced. Thus, less mercury loaded dust needs to be handled. The additional dedusting step in addition enhances a selective catalytic reduction of the main flue gas stream. This configuration is commonly referred to as 'low dust configuration'. In addition the mercury is oxidized as explained above and attaches better to the remaining dust.

[0031] In this application the terms 'upstream' and 'downstream' indicate a position relative to the direction of the flow of the flue gas, i.e. relative to the auxiliary flue gas stream or to the main flue gas stream. Beyond the word 'stream' and 'flow' have been used interchangeably to indicate that the respective gases are transported in conduits connecting the respective components of the clinker line. 'Stream' and 'flow' have sometimes been omitted for simplicity in parts of this application; or in other words, the terms 'stream' and 'flow' have been added to the terms flue gas and auxiliary flue gas, only if it appeared appropriate.

[0032] As indicated above, vaporization of mercury means a phase transition of metallic mercury or of mercury compounds (like $HgCL$, $HgCL_2$, $HgBr$, $HgBr_2$, ...) from a liquid or solid phase into a gas phase. Briefly the term 'mercury' unless explicitly stated means mercury in no matter which form (metallic, ionic, bound to a compound, ...). Condensation in turn is a phase transition from gas phase to a liquid or to a solid phase. The other heavy metals and their compounds show a similar behavior and can be removed essentially the same way, provided the respective boiling temperature is below temperature of the bypass gas.

[0033] The term filter is used herein only to indicate that dust (or other solid) matter is removed from a gas stream. It is generally irrelevant which process is used to separate the dust from gas. Lots of different techniques have been suggested and can be employed as required. Bag filters as well referred to as hose filters for example are cheap but not suited for dedusting hot gases. Ceramic filters, electrostatic precipitators and cyclones can be uses as well at elevated temperatures but have other drawbacks (higher installation and/or operational costs and/or a higher concentration of the remaining dust).

[0034] As indicated above, mercury loaded dust usually comprises as well other heavy metals like e.g. Thallium (Tl), Cadmium (Cd), lead (Pb) or the like (be it in elementary form or being bound in compounds). Heavy metals in general can be removed from the clinker process using the above explained method. In practice, the mercury content of the flue gas and the clinker is measured as an indicator of the total heavy metal content of the flue gas and the clinker, respectively. If the respective heavy metals are separated from the heavy metal loaded dust or not is essentially a question of the temperature of the auxiliary flue gas stream. In principle, one could thus replace the term 'mercury loaded dust' by 'heavy metal loaded dust'.

Description of Drawings

[0035] In the following the invention will be described by way of example, without limitation of the general inventive concept, on an example of embodiment with reference to the drawings.

Figure 1 shows a schematic sketch of a first cement clinker line.

Figure 2 shows a schematic sketch of a second cement clinker line.

Figure 3 shows a schematic flow diagram of an auxiliary flue gas stream.

[0036] The cement clinker line in Fig. 1 comprises as usual a preheater 2, a kiln 30 and a clinker cooler 4. Raw meal 8 is preheated in the preheater 2 and provided to the kiln inlet 31. In the kiln 30 the raw meal 8 is calcined and sintered to clinker. The clinker 9 is discharged on the clinker cooler 4 and can be further processed after being cooled down (indicated by an arrow, symbolizing the clinker 9), e.g. by milling. Hot air from the clinker cooler 4 is provided to the kiln 30 as secondary air and leaves the kiln 30 at its inlet 31 as flue or exhaust gas. Said kiln exhaust gas is dust loaded and hot (typically 1500°C to 2000°C). The main amount of the kiln exhaust gas (briefly 'main flue gas stream') is provided to the preheater 2 for pre-warming the raw meal 8. Optionally, a calciner 5 may be installed between the preheater 2 and the kiln 30. In that case the raw meal 8 is provided from the preheater 2 to the calciner 5 and from the calciner 5 to the kiln 30. At least a part of the kiln exhaust gas may be provided to the preheater via the calciner 5. Further, tertiary air may be provided from the clinker cooler 4 to the calciner 5.

[0037] A main fraction of the flue gas 38 exiting the preheater 2 is cooled down as indicated by a heat exchanger 10, representing simply some cooling means. The heat exchanger 10 enables to recuperate thermal energy when cooling the flue gas 38 and to use the thermal energy as process heat. But other cooling techniques like water cooling and the like may as well be used. Downstream of the cooling means, the main flue gas stream is next dedusted as indicated by dedusting means 130, 135 or used to pre-warm raw meal being produced in a raw-meal mill 15. The raw meal 8 provided by the raw-meal mill 15 is provided to the preheater 2. The raw-meal mill 15 can as well be heated by bypass gas 39 (after being processed to remove chlorides and the like) or other warm gases, as indicated by warm gas inlet 16.

[0038] Regardless whether the main flue gas stream 38 is used to heat the raw-meal mill 15 or if it bypasses the raw-meal mill 15, in any case it is dedusted at least by one of the dedusting means 130, 135, while having a temperature below the boiling point of mercury. The dust 110 being removed by said dedusting means, e.g. bag filters, comprises mercury as due to the cooling step indicated by reference numeral 10, the mercury is absorbed by the dust. At least a fraction of the mercury loaded dust 110 is entered to the preheater as indicated by arrow head 8, i.e. the corresponding fraction of the mercury is reintroduced as raw meal 8 into the preheater 2.

[0039] The cement clinker line in Fig. 2 is distinguishes from the cement clinker line of Fig. 1 only in the position of the branch off for the auxiliary flue gas stream 51. According to Fig. 1, an auxiliary flue gas stream 51 is drawn off at an the auxiliary flue gas branch off 40 between the preheater 2 and the subsequent heat exchanger 10, whereas in Fig. 2, the corresponding branch off 40 for drawing off the auxiliary flue gas stream 51 is an intermediate exit of the preheater 2. In the example of Fig. 2, the intermediate exit is connected with the main flue gas duct upstream (referring to the main flue gas flow) of the last cyclone (and downstream the corresponding upstream cyclone). But of course the number of cyclones and the position of the branch off 40 is only a preferred example and not intended to be limiting.

[0040] The branch off 53 provides an emergency flue gas outlet 52, preferably being connected to an emergency chimney. As shown in Fig. 1, it could be omitted as well, at least it is not relevant in the context of this invention

[0041] Fig. 3 shows an auxiliary flue gas branch of a cement clinker line. At least fraction, e.g. 1% to 30% or even more -if appropriate- of the kiln exhaust gas is drawn off as auxiliary flue gas stream 51 from the main flue gas stream downstream the preheater (2) (see Fig. 1) as indicated by branch off 40 (cf. Fig. 1) or by an intermediate outlet of the preheater 2, said intermediate outlet providing the as auxiliary flue gas stream 51 as shown in Fig. 2. From said branch off 40, the auxiliary flue gas stream 51 flows with a temperature of typically about 250°C to 450°C (possible are as well 200°C to 700°C) to the auxiliary flue gas branch. The auxiliary flue gas branch comprises a reductant injector 50 (as indicated by the dashed box 50) for injecting a reductant 55, like ammonia, ammonium or the like into the auxiliary flue gas stream 51. The dashed box indicates that the reductant injection is optional, but a preferred embodiment. The dust loaded, mercury containing auxiliary flue gas stream 51 is subsequently ducted to a hot gas filter 60 (as example for any suited dedusting means) to dedust the auxiliary flue gas stream (51) at a temperature T_1 still above the boiling point of mercury. Thereby, the dust is removed and the gaseous mercury remains gaseous and thus in the auxiliary flue gas stream. As indicated above, the hot gas filter 60 may comprise at least one catalyst for reducing nitrogen oxides to diatomic nitrogen and water. Alternatively the catalyst may be a separate unit as indicated by the dashed box 65. Thus, the auxiliary flue gas stream 51 is dedusted and (preferably) denitrified using a selective catalytic reduction (SCR), but as the temperature T_1 is still above the boiling temperature of the mercury, the mercury remains in the auxiliary flue gas stream 51. The catalyst changes the oxidation state of metallic mercury (Hg) to Hg^{+2} enhancing its subsequent absorption, as explained above. Next, the dedusted auxiliary flue gas stream 51 is cooled to a temperature T_2, e.g. in the order of 150°C to 200°C by a heat exchanger 68 or any other cooling means 68. Again, the dashed box indicates that the cooling means 68 is optional, but a preferred embodiment. If the cooling means 68 is a heat exchanger as indicated the heat removed from the auxiliary flue gas stream can be used as process heat, e.g. for an organic rankine cycle, a (pre-) heating a steam boiler or any other suited process.

[0042] Downstream of the optional cooling means 68 is a further branch 41 for optionally branching of at least a part of the dedusted but still mercury containing auxiliary flue gas stream. This branched stream 42 may be provided the exhaust 100 or used as gas for drying raw meal as indicated by 16. The remaining part of the auxiliary flue gas stream 51 (briefly auxiliary flue gas stream 51) is cooled to a temperature T_3 below the boiling temperature of mercury, preferably to about 70°C to 120°C.

[0043] After cooling the auxiliary flue gas stream (51) gas to T_3, an adsorbent 85 is injected into the auxiliary flue gas stream at 75 to adsorb the mercury and mercury compounds and preferably other heavy metals. Downstream of the injection, the adsorbent and thus the mercury is removed from the auxiliary flue gas using a filter 80, being an example for any suited dedusting means. The mercury loaded adsorbent 83 can be recirculated at least in part (see arrow 84). A further part 87 of the mercury loaded adsorbent is removed from the process and replaced by fresh adsorbent 86. The cleaned auxiliary flue gas stream leaving the filter 80 at 82 has a low dust concentration and a low mercury content. It can be used as process gas, e.g. for drying raw meal as indicated by 16. It can as well be released as indicated by 100 or used for cooling bypass gas 39.

[0044] The amount of mercury being removed from the process can be augmented, if mercury loaded dust 110, 111 is added to the auxiliary flue gas stream upstream of the hot gas filter 60. The mercury loaded dust can be provided from at least one of the dedusting means 130, 135. The auxiliary flue gas branch in addition enables to remove mercury from waste products 111 of other processes. 'Other processes' means here any process which is not a sub process of cement clinker manufacturing, e.g. the waste product can be waste material from landfill. For example mercury containing slag could be treated using the auxiliary flue gas branch, to thereby separate the mercury and reduce the amount of mercury contaminated waste to be deposited. Depending on the composition of the waste product 111 and the amount to be treated, the mercury free dust 63 (or more generally mercury free matter 63) can be provided together with the raw meal to the preheater. Alternatively the mercury free dust 63 can used as additive to the clinker.

List of reference numerals

[0045]

2
preheater

4
clinker cooler

5
calciner

6
tertiary air duct

8
raw meal

9
clinker

10
cooling means / heat exchanger (optional)

15
raw-meal mill

16
warm gas inlet

20
ventilation means

26
ventilation means

27
ventilation means

30
kiln

31
kiln inlet (raw meal inlet and flue gas outlet/ flue gas exhaust)

35
chloride bypass intake

38
main flue gas stream

39
chloride bypass gas

40
branch off (first)

41
branch off (second, optional)

42
branched fraction of auxiliary flue gas stream

50
reductant injector (optional)

51
auxiliary flue gas stream

52
emergency outlet (optional, can be connected to an emergency chimney)
53
emergency branch off (optional)
55
reductant
60
dust removal means
63
(essentially) mercury free dust/matter
65
catalyst unit (optional)
68
cooling means (optional), e.g. heat exchanger
70
cooling means, e.g. heat exchanger
75
adsorbent injecting means
80
dedusting means / adsorbent removal means
82
dedusted mercury free auxiliary flue
83
mercury loaded adsorbent
84
recirculated adsorbent
85
adsorbent
86
fresh adsorbent
87
removed adsorbent
100
exhaust
110
mercury loaded dust
111
mercury loaded waste product
130
dedusting means
135
dedusting means

REFERENCES CITED IN THE DESCRIPTION

Cited references

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- DE102011052561A1 [0008]
- EP2545337A [0015]

Non-patent literature cited in the description

- Der Herstellungsprozess**DR. HARDER**ZKG-Handbuch ZementanlagenbauBauverlag BV20130000vol. 2014, 20-37 [0002]
- **H.F.W. TAYLOR**Cement chemistryThomas Telford Publishing19970000 [0003]
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PATENTKRAV

1. Fremgangsmåde til fremstilling af klinker (9), hvilken fremgangsmåde omfatter i det mindste:

- sintring af råmel (8) til klinker (9) i en ovn (30),
- forvarmning af råmel (8) i en forvarmer (2) under anvendelse af en hovedrøggasstrøm (38) fra ovnen (30) som varmekilde,
- støvfjernelse i hovedrøggasstrømmen (38) nedstrøms for forvarmeren (2) ved en temperatur under kogepunktet for kviksølv, hvorved der tilvejebringes kviksølvholdigt støv (110),
- afgrening af en hjælperøggasstrøm (51) fra hovedrøggasstrømmen (38) ved en hjælpegasstrømsforgrening (40), før afkøling af hovedrøggasstrømmen (38) til under kogepunktet for kviksølv, hvor hjælperøggasstrømgrenen (40) afgrenes nedstrøms for forvarmeren (2) eller ved et mellemliggende gasudløb fra forvarmeren (2),
- støvfjernelse i hjælperøggasstrømmen (51), hvorved der tilvejebringes i det mindste i det væsentlige kviksølvfrit støv (63),
- binding af kviksølv fra hjælperøggasstrømmen til et adsorptionsmiddel (85), hvor bindingen omfatter injicering af adsorptionsmidlet (85) ind i den støvfjernede hjælperøggasstrøm (51) og afkøling af hjælperøggasstrømmen (51), og
- fjernelse af adsorptionsmidlet (87) fra hjælperøggasstrømmen (51) og yderligere bearbejdning af hjælperøggasstrømmen (51),

kendetegnet ved, at fremgangsmåden yderligere omfatter i det mindste:
- et reduktionsmiddel (55) injiceres i hjælperøggasstrømmen (51) og at hjælperøggasstrømmen (51) føres til en katalysator (60, 65) for denitrifikation af hjælperøggasstrømmen (51) opstrøms for bindingstrinnet.

2. Fremgangsmåde ifølge krav 1,
kendetegnet ved, at
fordampning af kviksølv ved injektion af i det mindste en fraktion af det kviksølvholdige støv (110) og/eller et kviksølvholdigt affaldsprodukt (111), ind i hjælperøggasstrømmen (39) og/eller ind i hovedrøggasstrømmen (38), opstrøms for hjælperøggasstrømsgrenen (40) for afgrening af hjælperøggasstrømmen (51).

3. Fremgangsmåde ifølge krav 1 eller 2,

kendetegnet ved, at

det kviksølvfrie støv (63) tilføres ovnen (4), for derved at opnå klinker (9).

4. Fremgangsmåde ifølge ethvert af de foregående krav,

kendetegnet ved, at

den støvfjernede hjælperøggasstrøm (51) tilføres en varmeveksler (68, 70) for opvarmning af et varmebærerfluid og i sin tur at afkøle den støvfjernede hjælperøggasstrøm (51) i bindingstrinnet.

5. Fremgangsmåde ifølge ethvert af de foregående krav,

kendetegnet ved, at

bindingstrinnet omfatter afkøling af hjælperøggasstrømmen (51) og efterfølgende injektion af adsorptionsmidlet (85) ind i hjælperøggasstrømmen.

6. Fremgangsmåde ifølge ethvert af de foregående krav,

kendetegnet ved, at

en første fraktion af det fjernede adsorptionsmiddel (83) injiceres ind i den støvfjernede hjælperøggasstrøm (39) og en anden fraktion af det fjernede adsorptionsmiddel (87) fjernes fra processen.

7. Fremgangsmåde ifølge ethvert af de foregående krav,

kendetegnet ved, at

støvfjernelse af hjælperøggasstrømmen (51) omfatter filtrering af i det mindste en fraktion af hjælperøggasstrømmen (51) under anvendelse af et katalytisk varmgasfilter, hvorved kviksølvatomer oxideres i hjælperøggasstrømmen (51) og nitrogenoxider (NO_x) konverteres til nitrogen (N_2).

8. Fremgangsmåde ifølge ethvert af de foregående krav,

kendetegnet ved, at

hovedrøggasstrømmen (38) køles nedstrøms for forvarmeren (2) og før dennes støvfjernelse.

9. Cementklinkerlinie omfattende i det mindste:

- en ovn (4) med en udblæsning (31) for udtrækning af en hovedrøggasstrøm (38),

- en forvarmer (2), som er forbundet med ovnen (4), for modtagelse af hovedgasstrømmen (51) fra hovedudblæsningen (38),

- første støvfjernelsesorganer (130, 135) til at fjerne støv fra hovedrøggasstrømmen (38) nedstrøms for forvarmeren (2) ved en temperatur under kogepunktet for kviksølv, for derved at tilvejebringe kviksølvholdigt støv,

- en gren (40) for afgrening af en hjælperøggasstrøm (51) med en temperatur over kogepunktet for kviksølv fra hovedgasstrømmen (38), hvilken gren (40) er nedstrøms for forvarmeren (2) eller er et mellemliggende gasudløb fra forvarmeren (2),

- andre støvfjernelsesorganer (60) nedstrøms for grenen (40) til at fjerne støv i hjælperøggasstrømmen (51) ved en temperatur over kogepunktet for kviksølv,

- køleorganer (68, 70) nedstrøms for de andre støvfjernelsesorganer (60), til afkøling af den støvfjernede hjælperøggasstrøm (51),

- adsorptionsmiddelinjektionsorganer (75) nedstrøms for de andre støvfjernelsesorganer (68, 70), til injicering af et adsorptionsmiddel (85) ind i hjælperøggasstrømmen (51), og

- adsorptionsmiddelfjernelsesorganer (80) nedstrøms for adsorptionsmiddelinjektionsorganerne (75) og nedstrøms for køleorganerne (68, 70),

kendetegnet ved, at

den yderligere omfatter i det mindste en katalysator (65) til denitrifikation nedstrøms for de første støvfjernelsesorganer (60) eller som er inkorporeret i de første støvfjernelsesorganer (60), og reduktionsmiddelinjektionsorganer (50) til injektion af et reduktionsmiddel (55) opstrøms for katalysatoren (65) ind i bypassrøggassen (39).

10. Cementklinkerlinie ifølge krav 9,

kendetegnet ved, at

den yderligere omfatter i det mindste fremføringsorganer til fremføring af i det mindste en fraktion af det kviksølvholdige støv (110), som udskilles af de første støvfjernelsesorganer (130, 135) og/eller for et kviksølvholdigt affaldsprodukt (111), til støvinjektionsorganer til injicering af fraktionen af det kviksølvholdige støv (110) i det mindste delvis ind i hjælperøggasstrømmen (51), hvorved kviksølv indeholdt i den nævnte fraktion af det kviksølvholdige støv (110) og/eller affaldsproduktet (111), fordampes i hjælperøggasstrømmen (51) og/eller i hovedrøggasstrømmen (39), opstrøms for grenen (40).

11. Cementklinkerlinie ifølge krav 10,

kendetegnet ved, at

den yderligere omfatter i det mindste fremføringsorganer til fremføring af i det mindste en fraktion af det fjernede adsorptionsmiddel (83) til adsorptionsmiddelindgangen til adsorptionsmiddelinjektionsorganerne (75).

12. Cementklinkerlinie ifølge ethvert af kravene 9 til 11,

kendetegnet ved, at

den yderligere omfatter i det mindste én forbindelse til at indføre det kviksølvfrie støv (63) ind i ovnen (4).

13. Cementklinkerlinie ifølge ethvert af kravene 9 til 12,

kendetegnet ved, at

køleorganerne omfatter en varmeveksler (68, 70) til overføring af varme fra hjælperøg-gasstrømmen (51) til et varmebærerfluid.

DRAWINGS

Fig. 1

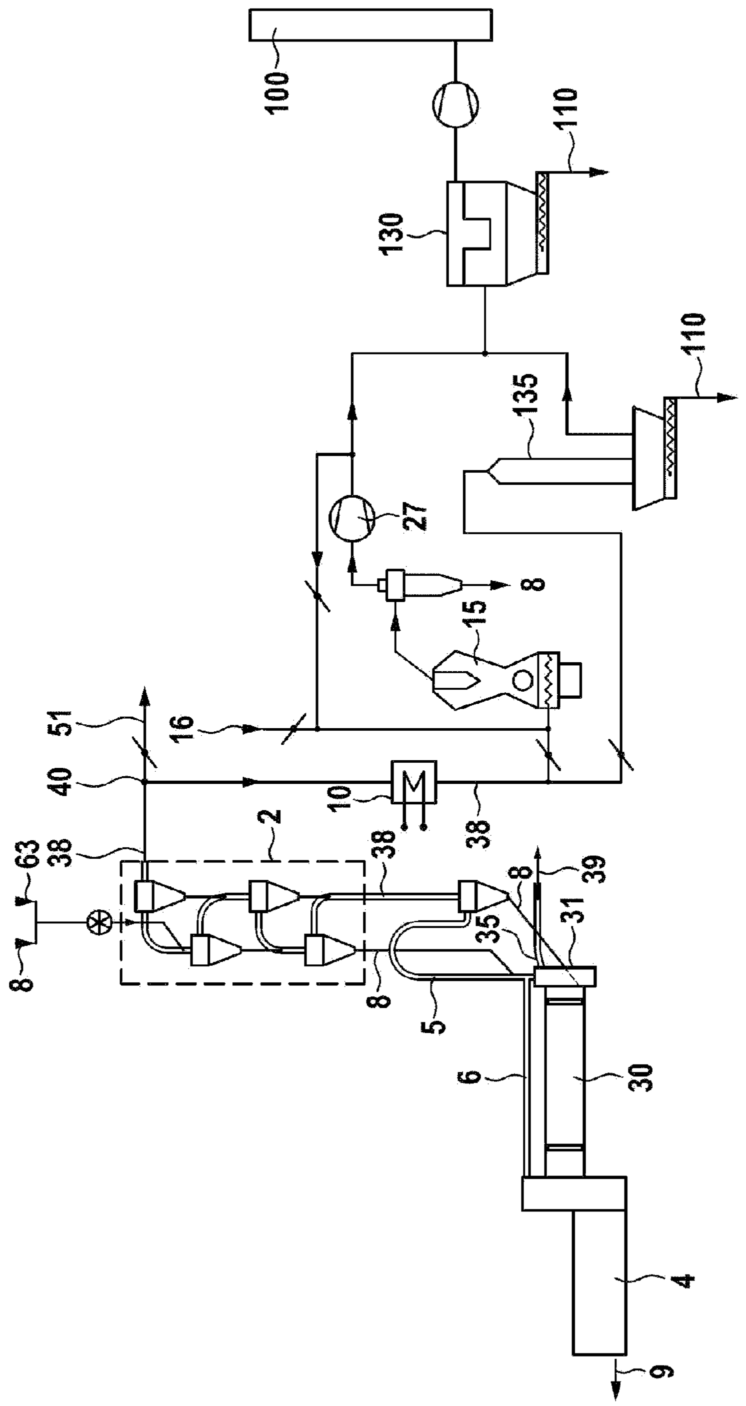
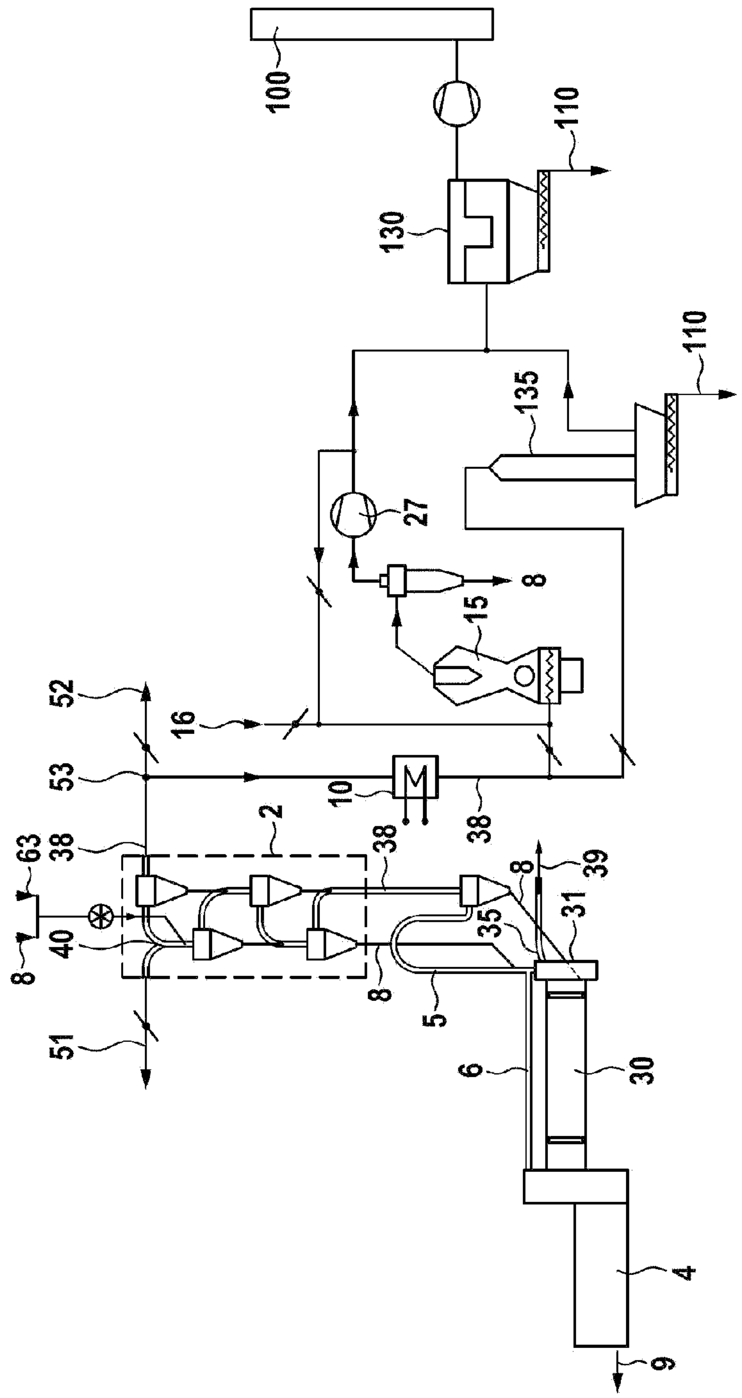


Fig. 2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110
130
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135
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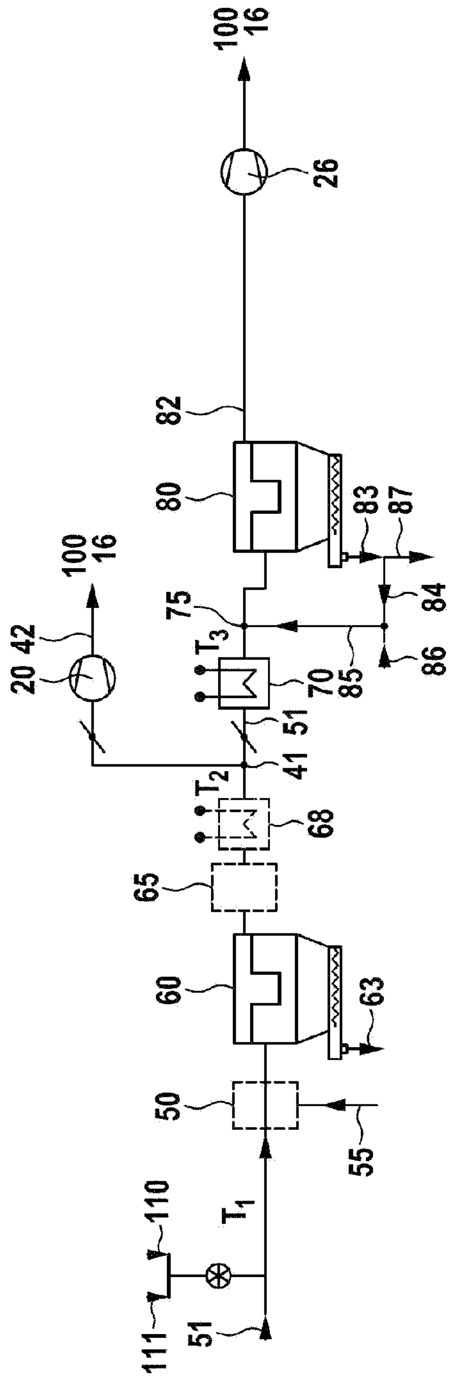
8
15
52
16
53
10
38
63
38
2
38
8
39
8
40
31
35
8
5
51
6
30
4
9

Fig. 3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26
82
80
83
87
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85
75
T_3
70
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41
T_2
68
65
60
63
50
55
T_1
110
111
51
20
42
100
16