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(54) Benævnelse: **Fremgangsmåde til rensning af forbrændingsrøggasser**

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The present invention relates to a method and facility for purifying fumes resulting from the combustion of waste products or fossil fuels.

Like the generation of energy by the combustion of fossil fuels, the incineration of waste products is of major interest to modern societies. In both cases, the combustion process generates fumes that are too highly laden with pollutants for them to be discharged back into the atmosphere without treatment. These fumes contain in particular sulphur oxides, including sulphur dioxide (SO_2) and sulphur trioxide (SO_3), halogenated acids, in particular hydrochloric acid (HCl), dusts, heavy metals and organic compounds of varying toxicity, as well as nitrogen oxides.

Several technologies are used to purify these fumes of their pollutants.

Wet systems, in which the fumes to be treated are brought into contact with a neutralising liquid, are a method of choice for energy production plants. These processes are very effective, but costly in investment and generate waste water that must be treated. This discharge back into the environment is not always possible even after treatment.

Semi-dry processes, in which a liquid laden with a neutralising reagent is atomised in a spray tower and the dry residue of the reaction as well as the other solids are recovered in a filter or an electrofilter, avoid water emission. These semi-dry processes are effective, but, since the fumes must be at a sufficiently high temperature to allow the spraying process, energy recovery is limited. In other words, the energy production is no longer as extensive as it could be. Moreover, the spray reactors are bulky and have a large footprint.

Dry processes, in which the fumes to be treated are brought into contact with a reagent in powder form, which will react with the acid pollutants, and in which the product of the reaction as well as the other solids are collected in a bag filter or an electrofilter, are effective and relatively inexpensive in investment. However, the reaction between the neutralising reagent and the acid gases, such as sulphur dioxide and hydrochloric acid, is incomplete. A significant excess amount of reagent is necessary. This results in a more significant quantity of reagent being consumed than in the case of semi-dry processes or wet processes as well as a significant volume of residues being collected by the filter or electrofilter. These residues have a toxic nature and their discharge cost is high. Since the reagent is not completely spent,

therefore, the aim is to reuse it by recirculation after having reactivated it. Thus, documents US-B-6 213 629, FR-A-2 883 772 and FR-A-2 911 518 propose arrangements for recirculating, reprocessing and/or humidifying these residues.

In particular, FR-A-2 883 772 proposes a process for reactivation by steam, which enables performance rates to be significantly improved in relation to a simple recirculation. Other improvements aiming to cause a partial condensation of water on the reagent are proposed, e.g. in DE-B-10 2005 058173, but only reprocess the fresh product and not the whole with the recirculated reagent.

Moreover, traditionally, the dry method processes use slaked lime ($Ca(OH)_2$) as neutralising reagent, which is more expensive than quick lime (CaO) that is used more commonly in semi-dry or wet processes with the preparation of a milk of lime.

For its part, WO-A-2004/026443 proposes to mix solid residues separated from fumes to be purified with quick lime, providing a first forced cooling phase of this mixture using air and water, then a second phase of wetting using steam, which is particularly short with a maximum duration of 30 seconds.

The aim of the present invention is to propose an improved method and facility for dry purification, in which the consumption of reagent is reduced.

For this, the invention relates to a method for purifying combustion fumes, as defined in claim 1.

The idea forming the basis of the invention is to activate recirculated residues by incorporating alkaline earth metal oxide and exposing the resulting reaction mixture to a gaseous flux containing steam at the same time. Conducting this activation over a sufficient period surprisingly saw significant reactivation performance rates even for low quantities of alkaline earth metal oxides. Of course, insofar as the objective of the invention is to reactivate the recirculated residues to the maximum extent, it is understood that the reaction mixture of the aforementioned solids and its exposure to steam are advantageously conducted at the highest possible temperature available. Therefore, no forced cooling of the solids is provided before their exposure to steam, for example. In this way, the chemical reactivation

reactions benefit thermally, especially with respect to their kinetics, and result in real reorganisation effects on the solid chemical structures, in particular at the level of the material particles, particularly by bursting, cracking etc. In other words, the invention promotes the reactivation of the solids by restructuring and slow solid-solid reactions furthered by the temperature.

Additional advantageous characteristics of the method according to the invention, taken alone or in all technically possible combinations, are specified in dependent claims 2 to 10.

The invention will be better understood on reading the following description given solely by way of example and with reference to Figure 1, which schematically shows a purification facility according to the invention.

In Figure 1 fumes to be purified 1 coming from a combustion unit such as a waste incinerator or an energy production plant and containing acid pollutants such as sulphur dioxide and/or hydrochloric acid are fed into a gas-solid separator 101 after mixing with a flux 7, which will be explained in detail below.

The mixture 1' of the fumes to be treated 1 and the flux 7 has a temperature in the range of between 110° and 230°C, preferably between 130° and 160°C, when it enters the separator 101.

As an option (not shown), at least one heat exchanger such as an evaporator or energy recuperator that is not the subject of the invention can be present and assist in lowering the temperature of the mixture 1' before it is fed into the separator 101.

In practice, a separator 101 is a technology known per se. This separator is preferably a bag filter. In a variant it can also be an electrofilter or similar device.

Both purified fumes 2 and solid residues 3containing, amongst other things, the solids present in the fumes to be purified 1, in particular fly ash, are recovered at the outlet of the separator 101.

Part 4 of the collected solid residues 3 is evacuated, while the remaining part 5, which represents between 50% and 95% of the total flow of the residues 3, is directed to a quench reactor 102.

According to the invention a neutralising reagent 6 formed from alkaline earth metal oxide, preferably quick lime (CaO) and/or magnesium (MgO), is also fed into the reactor 102. The quantity of reagent 6 feeding the reactor 102 advantageously represents between 2% and 25% by mass of the total quantity of solids admitted therein and preferably between 5% and 10% by mass.

Optionally, and not shown in Figure 1, a quantity of this or these alkaline earth metal oxides forming the reagent 6 is fed in immediately upstream of the separator 101 being mixed with the mixture 1'.

Also optionally, in addition to the alkaline earth metal oxide(s) reagent 6, other solid constituents can be fed into the reactor 102, in particular as a non-restrictive example activated carbon, lignite coke, clays, zeolites and/or slaked lime.

According to the invention a gaseous flux 8 containing between 25% and 100% by volume of steam is also fed into the reactor 102.

In these conditions known chemical reactions then occur in the reactor 102, including the following reactions:

(a) $Cao + H_2O \rightarrow Ca(OH)_2$

(b) $CaCl_2 + Ca(OH)_2 \rightarrow 2Ca\ Cl(OH)$, and

(c) $CaCl_2 + CaO + H_2O \rightarrow 2Ca\ Cl(OH)$.

Some of these reactions, in particular reaction a, are highly exothermic and can help cause the solid particles to burst and thus regenerate their surface. At the same time some of these reactions, in particular reaction b, produce a phenomenon of reactivation and regeneration of the solid residues. Unexpectedly, the contribution of the alkaline earth metal oxide compounds forming the reagent 6, such as quick lime, has a significant beneficial effect on the activity of the reactivated reagents, probably linked to the capacity of these alkaline earth metal oxides to release a substantial amount of heat at the surface of the particles. In other

words, the reactivation in the presence of alkaline earth metal oxide is much more effective than reactivation without it, as when it is done simply with steam or done with steam and, for example, added slaked lime, i.e. calcium hydroxide ($Ca(OH)_2$).

According to the invention the reactor 102 is a gas-solid contactor, which assures a flow time of the solids in the range of between 1 and 30 minutes, preferably between 5 and 10 minutes, or also preferably between 3 and 8 minutes. In practice, the reactor 102 is a known technology and can preferably be formed from an endless screw, a rotary drum or a fluidised bed. On entering the reactor 102, the gas of the flux 8 is possibly distributed along the abovementioned screw.

The thus reactivated solid residues leaving the reactor 102 form the abovementioned flux 7 and are recycled to the separator 101. In that way, in the mixture 1' the acid pollutants of the fumes to be treated 1 react with the reactivated residues coming from the reactor 102, in particular by being fixed by these reactivated residues and mixing with the solids initially present in the fumes 1.

Optionally, at least a portion of the gases leaving the reactor 102 is also recycled to the separator 101 serving as carrier gases for the solid flux 7. These recycled gases are formed, for example, by a fraction of the flux 9 that has not reacted in the reactor 102.

Patentkrav

1. Fremgangsmåde til rensning af forbrændingsrøggasser, hvor:

- røggasser, som skal renses (1), sendes gennem en separator af gas og faste stoffer (101),
- der indføres ved indgangen af en aktiveringsreaktor (102) på én gang:
  - en fraktion (5) af de faste reststoffer (3), som kommer fra separatoren (101), hvor denne fraktion ligger mellem 50 og 95% af den samlede gennemstrømningsmængde af de faste reststoffer (3), som kommer fra separatoren,
  - et reagens (6), som består af jordalkalikaoxid, og
  - en gasstrøm (8), der indeholder mellem 25 og 100 volumen% vanddamp,

  hvor de faste stoffers gennemløbstid i reaktoren (102), mens blandingen af fraktionen af faste reststoffer (5) og reagenset (6) udsættes for gasstrømmen (8), ligger mellem 1 og 30 minutter, og
- de faste stoffer (7), som kommer fra reaktoren (102), føres tilbage til separatoren (101) ved at blande dem med de røggasser, der skal renses (1) opstrøms for separatoren.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** de faste stoffers gennemløbstid i reaktoren (102) ligger mellem 5 og 10 minutter.

3. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** de faste stoffers gennemløbstid i reaktoren (102) ligger mellem 3 og 8 minutter.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** reagenset (6), som består af jordalkalikaoxid, er ulæsket kalk.

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** reagenset (6) som består af jordalkalikaoxid, er magnesia.

6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** der ud over de faste stoffer (7), som kommer fra reaktoren

(102), indføres et reagens, som består af jordalkalikaoxid, i de røggasser, der skal renses (1), opstrøms for separatoren (101).

7. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** der desuden tilføres aktivt kul, brunkulskoks, ler, zeolitter, læsket kalk eller en blanding af disse forbindelser i reaktoren (102).

8. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** mængden af reagenset (6), som føres ind i reaktoren (102), udgør mellem 2 og 25% af den samlede mængde af de faste reststoffer, som tilføres deri, fortrinsvis mellem 5 og 10%.

9. Fremgangsmåde ifølge et hvilket som af de foregående krav, **kendetegnet ved, at** separatoren (101) er et posefilter.

10. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** reaktoren (102) er en skrue uden ende, en roterende tromle eller et fluidiseret leje.

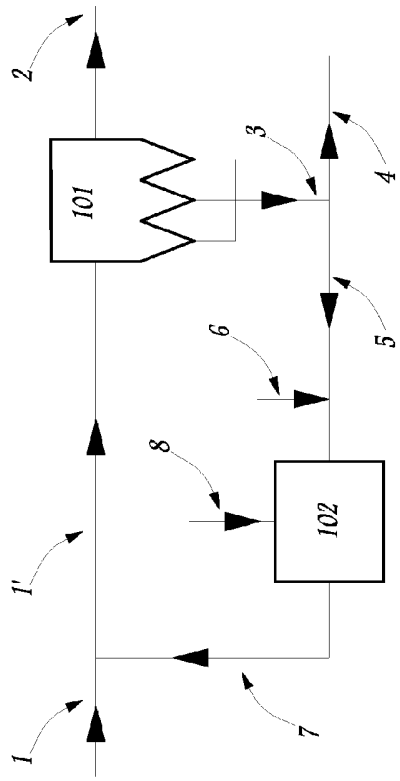


Fig.1