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(54) Title: METHOD OF REMOVING MERCURY FROM COMBUSTION EXHAUST GASES

(57) Abrégé/Abstract:

The present invention relates to a method of removing mercury from combustion exhaust gases from combustion plants, such as power stations or waste combustion plants. Previous methods for removing mercury from combustion exhaust gases are structurally complex and cost intensive. The object resulting from this problem is solved by a method, in which the mercury-containing combustion exhaust gases are brought into contact with an adsorption agent, whereby the mercury is substantially adsorbed by the adsorption agent during this contact. After the adsorption has occurred the adsorption agent is separated from the combustion exhaust gases and added to an aqueous solution containing an oxidising agent, whereby the adsorbed mercury goes into solution as Hg^{2+}. The Hg^{2+}-containing solution is subsequently separated from the adsorption agent and the Hg^{2+} is then removed from the solution. This conduct of the method enables the mercury to be removed from the combustion exhaust gases in a simple and economical manner.

ABSTRACT

The present invention relates to a method of removing mercury from combustion exhaust gases from combustion plants, such as power stations or waste combustion plants. Previous methods for removing mercury from combustion exhaust gases are structurally complex and cost intensive. The object resulting from this problem is solved by a method, in which the mercury-containing combustion exhaust gases are brought into contact with an adsorption agent, whereby the mercury is substantially adsorbed by the adsorption agent during this contact. After the adsorption has occurred the adsorption agent is separated from the combustion exhaust gases and added to an aqueous solution containing an oxidising agent, whereby the adsorbed mercury goes into solution as Hg^{2+}. The Hg^{2+}-containing solution is subsequently separated from the adsorption agent and the Hg^{2+} is then removed from the solution. This conduct of the method enables the mercury to be removed from the combustion exhaust gases in a simple and economical manner.

Method of removing mercury from combustion exhaust gases

The present invention relates to a method of removing mercury from combustion exhaust gases.

Exhaust gases from combustion installations, such as power stations or waste combustion plants, contain a number of pollutants, which must be removed from the combustion exhaust gases before they are discharged to the environment. Modern combustion plants are equipped with exhaust gas cleaning devices, which remove inter alia sulphur dioxide, nitrogen oxides, hydrogen halides and entrained ash contained in the combustion exhaust gases.

In addition to the pollutants referred to above, the combustion exhaust gases contain traces of heavy metals, which must be removed from the combustion exhaust gases due to their toxicity. One particularly poisonous heavy metal contained in the combustion exhaust gases is mercury. This is washed out of the combustion exhaust gases in conventional exhaust gas desulphurisation devices (EGD) and flows with the waste water from the exhaust gas desulphurisation devices into the waste water plant. The mercury dissolved in the waste water is precipitated in the waste water plant in low-solubility form together with other solid materials in the form of exhaust gas waste water plant (EGW) slurry. As a result of the contamination with mercury, this EGW slurry can, however, not be burnt but must be disposed of as special waste.

EP 0 792 186 B1 discloses a method of cleaning combustion exhaust gases, with which mercury can be removed from the combustion exhaust gases. For this purpose, the combustion exhaust gases are subjected to a wet washing process, wherein this wet washing process is conducted with the addition of activated carbon particles, which absorb the heavy metals and, in particular, mercury. The activated carbon particles are then separated from the suspension produced in the wet washing process and recirculated into the wet washing process, whereby a proportion of the particles is tapped off and thermally desorbed. The thermal desorption is complex as regards installation technology and is thus cost intensive.

It is therefore the object of the invention to provide a simple and economical method of removing mercury from combustion exhaust gases.

The object is solved by a method in which mercury contained in the combustion exhaust gases is firstly brought into contact with an adsorption agent, whereby the mercury is substantially adsorbed by the adsorption agent. In the context of this application, the use of the term "mercury" includes mercury in the 0, 1 and 2 oxidation levels.

In the method in accordance with the invention, the adsorption agent can, for instance, be blown into the combustion exhaust gases in the form of fine particles. In such an event, the mercury is adsorbed substantially directly by the adsorption agent from the combustion exhaust gases. The adsorption agent can also be added in a wet working step, such as desulphurisation. In this case, the mercury contained in the combustion exhaust gases goes firstly partially into solution and is substantially adsorbed from the latter by the adsorption agent. It is also possible to combine adsorption from the gas phase and from liquid by introducing the adsorption agent into the combustion exhaust gases upstream of a wet working step.

The common adsorption agents, such as bentonite, silica gel and activated carbon, can be used as the adsorption agent.

The adsorption agent is separated from the combustion exhaust gases after the adsorption. Such separation can be conducted with all the devices known to a person skilled in the art.

After the adsorption agent loaded with mercury has been separated from the combustion exhaust gases, it is brought into contact with an aqueous solution containing an oxidising agent.

It has now been found surprisingly that with such a treatment of the adsorption agent, the mercury can be almost quantitatively separated from it and goes over into the aqueous solution in the form of Hg^{2+}. Heating of the aqueous solution is not necessary, whereby this working step can be implemented very economically.

The present method is not limited to a specific oxidising agent. For instance, hypochlorite, chlorine dioxide or chlorine gas can be used. It is also possible to release the mercury from the adsorption agent by catalytic oxidation with air, optionally in the presence of a Cu^{2+} salt. The use of hypochlorite is particularly preferred since it is simple to handle, and is economically available in large amounts by comparison with gaseous oxidising agents. It has further transpired that when using hypochlorite, only a short residence time of the adsorption agent in the aqueous solution is necessary in order to relax the mercury from the adsorption agent.

Since certain oxidising agents operate only in certain pH ranges, a pH range can be set, which is the most favourable for subsequent working steps, by appropriate choice of the oxidising agent in this step of the method.

After the mercury has been released from the adsorption agent, the Hg^{2+}-containing solution is separated from the adsorption agent and further solid materials which are potentially present. The mercury content of the adsorption agent and of potentially present further solid materials is now so low that they can, for instance, be burnt.

After separating the adsorption agent, the mercury is removed from the solution. The removal of the mercury from the solution can be performed with any method known to the expert.

The method in accordance with the invention has a number of advantages by comparison with known methods. On the one hand, the waste water produced in the treatment of the combustion exhaust gases, for instance from an EGD washer, is contaminated with mercury to a very small extent only because, as a result of the addition of the adsorption agent, the mercury goes over to it. This results in the EGW slurry produced in a subsequent waste water installation not being contaminated with mercury and this therefore not having to be disposed of as special waste but can instead be burnt. Furthermore, the mercury can be separated again from the adsorption agent with a solution including an oxidising agent in a manner which is simple as regards installation technology and is thus economical and after this separation it can be removed from the solution with a known method.

The Hg^{2+} can be removed from the solution in a manner which is particularly economical and uncomplicated as regards installation technology by adding to the Hg^{2+}-containing solution a precipitating agent, which forms a low solubility precipitate with Hg^{2+} and separating it from the solution. Sulphides, and particularly organosulphides, are preferred as the precipitating agents. The mercury sulphide which forms in the reaction with the precipitating agent is resistant over a wide pH range and can be further used as a pigment. It is also advantageous that mercury sulphide is practically insoluble in water and is thus classified as non-poisonous. The use of organosulphides is particularly preferred since they form with the mercury "larger" organomercury sulphide molecule, in comparison to pure mercury sulphide, which precipitate more easily out of the corresponding solution. The smaller the mercury content of the exhaust gases, the more is the use of organosulphides to be recommended in order thus to enable as low as possible a mercury content of the cleaned waste water.

Alternatively, the Hg^{2+} can be removed from the solution by bringing the solution into contact with an ion exchanger. This manner of removing the mercury from the solution is also simple to implement as regards installation technology.

Various IMAC™ variants or 1, 3, 5-triazine-2,4,6-trithiol can be used as the ion exchange resin. The method in accordance with the invention is, however, not limited to these resins. Ion exchange resins with functional H-S groups are particularly preferred since particularly efficient removal of the mercury from the solution is possible with them.

In a preferred embodiment of the invention, Hg^0 contained in the combustion exhaust gases is oxidised before bringing the mercury contained in the combustion exhaust gases into contact with the adsorption agent. Since the adsorption agents preferably adsorb Hg^{2+}, the Hg concentration in the cleaned combustion exhaust gases can be further reduced by oxidation of Hg^0 contained in the combustion exhaust gases. Such oxidation is, however, only necessary and sensible if the Hg^0 content of the combustion exhaust gases is too high. The oxidation of the Hg^0 can, for instance, be effected by catalysts or halogens but other method steps for oxidising the Hg^0 known to the expert are also possible.

When cleaning the combustion exhaust gases, they are, amongst other things, desulphurised. This desulphurisation occurs in so called EGD washers, in which the sulphur dioxide contained in the combustion exhaust gases is converted into a sulphate in the presence of an oxidising agent. The sulphate is separated and - depending on the desulphurisation process - further processed or dumped. This separation step can also be used for separating the adsorption agent from other solid materials by supplying the adsorption agent to the combustion exhaust gases before or in the EGD washer. The separation of the sulphate can be combined in this manner with the separation of the adsorption agent, which reduces the additional complexity as regards installation technology and thus the cost. This separation may be implemented particularly simply if the solid materials produced in the EGD washer are separated from the adsorption agent by centrifugal separation. Two phases are produced with such separation. One is the heavy crystalline calcium sulphate and the other is a waste water suspension, which contains, amongst other things, the adsorption agent and further solid materials, particularly metal hydroxides. After the gypsum has been separated, the adsorption agent is separated, together with the other solid materials, from the waste water.

Since activated carbon has a particularly large active surface area and thus need be added to the combustion exhaust gases only in very small quantities, activated carbon is preferably used as the adsorption agent. The use of activated carbon further has the advantage that it can be simply separated in the subsequent working step. Furthermore, after bringing it into contact with a solution containing an oxidising agent, the activated carbon can be burnt without difficulty with other solid materials to be removed.

The use of activated carbon produced from peat is particularly advantageous since it has a larger internal surface area compared to other types of activated carbon.

In combustion installations, in which large volumes of combustion exhaust gases are produced, for instance in power stations, it is advantageous that the adsorption agent is separated and recirculated after bringing it into contact with a solution containing an oxidising agent. The procurement costs for the adsorption agent may be reduced in this manner and the environmental impact produced by burning the adsorption agent is prevented.

The invention will be described in more detail below by way of a preferred exemplary embodiment of the method in accordance with the invention in conjunction with the attached drawing. The drawing is a flow diagram of an exemplary embodiment of the method in accordance with the invention.

The exemplary embodiment of the method in accordance with the invention shown in the flow diagram relates to the combustion exhaust gas cleaning for a 500MW block of a power station.

The combustion exhaust gases flow from the combustion device (1) to the denitrogenation device (2), with which the nitrogen oxides are removed from the combustion exhaust gases. The denitrogenation device can be operated in accordance with a method known to a person skilled in the art, such as selective non-catalytic or catalytic denitrogenation.

The exhaust gases from which nitrogen has been removed flow into a dust removal plant (3), in which suspended dust is removed from the combustion exhaust gases. For the purpose of dust removal from the combustion exhaust gases, an electrostatic filter is generally used in power stations.

The precise method used for the denitrogenation and dust removal has, however, no influence on the present invention - these two working steps are merely shown for the sake of completeness.

After the removal of dust from the combustion exhaust gases, they flow into the desulphurisation plant or EGD washer (4). In the illustrated exemplary embodiment of the method in accordance with the invention, the sulphur dioxide in the combustion exhaust gases is removed with a spray absorption method, in which a basic slaked lime suspension is sprayed into the combustion exhaust gases to be cleaned. The $CaSO_3$ produced in the reaction with sulphur dioxide is oxidised, for instance with atmospheric oxygen, to form $CaSO_4$. In this oxidation process, Hg^{1+}, which is potentially still present in the combustion exhaust gases, is oxidised to Hg^{2+}. In alternative exemplary embodiments, other desulphurisation methods can be used - for instance desulphurisation with ammonia.

Activated carbon particles constituting an adsorption agent are added to the so called sump of the EGD washer (4). The activated carbon particles adsorb the Hg^{2+} which has passed over from the combustion exhaust gases into the EGD washer solution. In alternative exemplary embodiments, it is, for instance, possible to blow fine activated carbon particles into the combustion exhaust gases upstream of the EGD washer. In such an event, a proportion of the mercury present in the combustion exhaust gases is already adsorbed by the activated carbon particles from the combustion exhaust gases themselves. The mercury which is not adsorbed goes into solution in the EGD washer and is adsorbed there by the activated carbon particles.

In a 500MW combustion plant, about 1.5 million m^3 combustion exhaust gases are produced per hour. With a mercury content of < 0.50 mg per kilo carbon, only about 4 kg of activated carbon need be added per hour. The concentration of the activated carbon particles with such a rate of addition is about 100 mg/l in the EGD washer. The suspension produced in the EGD washer, which contains inter alia gypsum, further solid materials and activated carbon particles, is conducted into a gypsum cyclone 5, which separates the suspension produced in the EGD washer into two phases, namely the heavy crystalline $CaSO_4$ and a suspension, which contains the light activated carbon particles and further amorphous and thus light solid materials, such as dust and metal hydroxides. The degree of whiteness of the gypsum is only insignificantly reduced by the addition of activated carbon, namely from about 74% to 72%.

The suspension leaving the gypsum cyclone (5) is conducted into a waste water cyclone (6). A proportion of the waste water is separated from the suspension in this waste water cyclone (6) and a suspension is produced with a higher solid material content. The volume of this suspension from the waste water cyclone (6) is substantially reduced by comparison with the suspension from the gypsum cyclone (5) so that subsequent method steps can be of less expensive design as regards installation technology.

The waste water leaving the waste water cyclone (6) has a mercury concentration of only about 10 μg/l. The waste water is in part recirculated into the method or it is supplied to a waste water plant. As a result of the low mercury content the EGW slurry produced in the waste water plant can be burnt - dumping is no longer necessary.

The method in accordance with the invention is, however, not limited to the separation of the activated carbon and other solid materials from the waste water or the combustion exhaust gases as described in this exemplary embodiment. In addition to the use of a gypsum cyclone and a waste water cyclone, the separation can also be effected with other separation methods known to a skilled person in the art. The above separation method is, however, preferred since it enables separation into gypsum, waste water and a suspension containing solid materials with simple means.

In a subsequent method step, an aqueous sodium hypochlorite solution with a pH value of ca. 6.5 is introduced into the suspension from the waste water cyclone (6), which contains the activated carbon particles and further solid materials. 1-4 ml of a ca. 13% sodium hypochlorite solution is introduced per litre of suspension. In order to prevent deposition of the solid materials at this time, the solution is mixed with a suitable stirring device. In alternative exemplary embodiments, other oxidising agents in a different pH range can of course be used. During the treatment with the oxidising agent, the mercury is released from the activated carbon and goes into solution as Hg^{2+}.

After the mercury has gone completely into solution, which depends on the activated carbon which is used and the concentration of the oxidising agent and on the temperature, the solution is mixed with a flocculating adjuvant and/or a flocculating agent and, in order to increase the pH value of the solution, with $Ca(OH)_2$. The solution is thus adjusted to a pH value of about 8.5. The increase in the pH value occurs on the one hand by reason of legal requirements, which state that waste water from a waste water cleaning plant must have a pH value lying within a certain pH value window, and, on the other hand, to ensure gypsum desaturation of the solution. This means that when the $Ca(OH)_2$ is added, further calcium sulphate is precipitated from the solution. Furthermore, when the pH value is increased, further metal hydroxides, such as nickel and copper hydroxide, precipitate out of the solution. The term flocculating agents is to be understood as those substances which so influence the particles in a suspension that they aggregate into flakes (microflakes) and can thus be removed from the suspension. Iron(III) chloride, iron (III) sulphate or a mixture of these salts is preferably used as the flocculating agent in the present exemplary embodiment. Which of these salts is used depends on their current availability. When the salts are added, a voluminous $Fe(OH)_3$ precipitate is produced, which agglomerates with other less voluminous solid materials. In order to accelerate the speed of deposition of the aggregated particles and to simplify separation of them, a so called flocculating adjuvant can be added, which brings about the agglomeration of solid material particles into larger units (macroflakes), which can precipitate more rapidly due to their larger mass and can be separated more simply. Anionic polymers are preferably added as the flocculating adjuvant in the present exemplary embodiment. Whether and in what amount a flocculating agent or a flocculating adjuvant is added, depends on the composition of the suspension and thus on the conduct of the method and the composition of the combustion exhaust gases.

The solid materials obtained in the suspension in the above treatment, which are now substantially free of mercury, are subsequently separated from the mercury-containing solution in a filter press. In the presently described exemplary embodiment, about 20 tonnes of solid materials are produced per day, in which the mercury content is less than 10 g/t. As a result of this low mercury content, the solid materials can be burnt and no costs thus arise for dumping. In another exemplary embodiment, the solid materials can also be separated by sedimentation or flotation.

In order to precipitate the mercury, the mercury-containing solution is mixed with an organosulphide, a flocculating agent and a flocculating adjuvant. Iron (III) chloride is preferably used as the flocculating agent since this is economically available. An oxidation-resistant organosulphide is preferably used as the organosulphide since the solution can have a high oxidation potential. In order to prevent deposition of the mercury organosulphide at this time, the solution is mixed at this stage with a suitable stirring device. After the mercury has been precipitated in the form of a mercury organosulphide, the solid materials are separated by means of a membrane filter press and dumped. In the presently described exemplary embodiment, about 0.2 t mercury organosulphide-containing waste is produced per day.

Claims

1. Method of removing mercury from combustion exhaust gases including the following steps:

a) bringing mercury contained in the combustion exhaust gases into contact with an adsorption agent, whereby the mercury is substantially adsorbed by the adsorption agent,

b) separating the adsorption agent from the combustion exhaust gases,

c) bringing the adsorption agent into contact with an aqueous solution containing an oxidising agent, whereby the adsorbed mercury goes into solution in the form of Hg^{2+},

d) separating the Hg^{2+}-containing solution from the adsorption agent, and

e) removing the Hg^{2+} from the solution.

2. A method as claimed in claim 1, characterised in that the Hg^{2+} is removed from the solution by mixing the Hg^{2+}-containing solution with a precipitating agent, which forms with the Hg^{2+} a low solubility precipitate and separating the latter from the solution.

3. A method as claimed in claim 2, characterised in that an organosulphide is used as the precipitating agent.

4. A method as claimed in claim 1, characterised in that the Hg^{2+} is removed from the solution by bringing the solution into contact with an ion exchanger.

5. A method as claimed in one of claims 1 to 4, characterised in that the Hg^0 contained in the combustion gases is oxidised before bringing mercury contained in the combustion exhaust gases into contact with the adsorption agent.

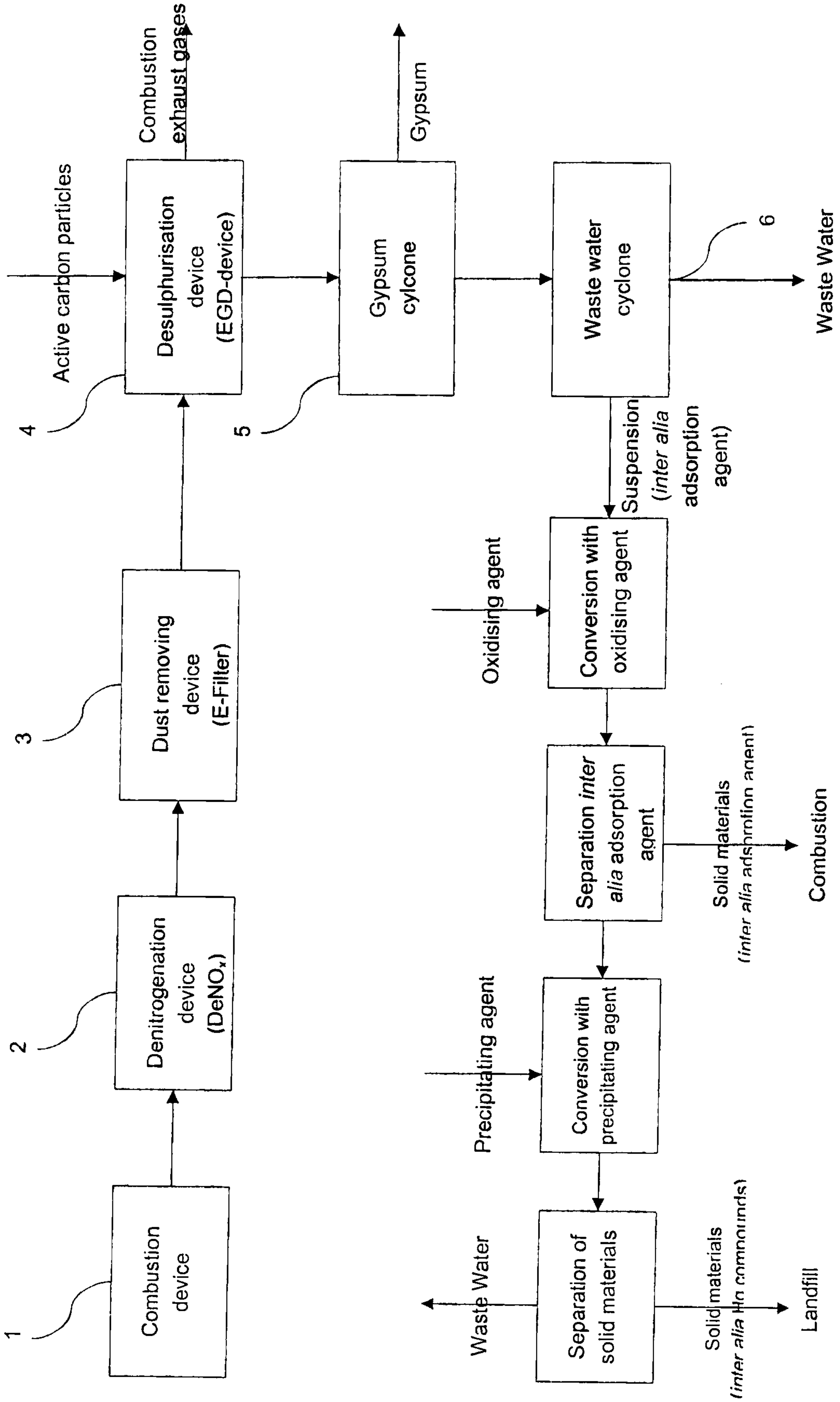
6. As method as claimed in one of claims 1 to 5, characterised in that the adsorption agent is added to the combustion exhaust gases before or in an exhaust gas desulphurisation device.

7. A method as claimed in claim 6, characterised in that solid materials produced in the exhaust gas desulphurisation device are separated from the adsorption agent by centrifugal separation.

8. A method as claimed in one of claims 1 to 7, characterised in that hypochlorite, chlorine dioxide or chlorine gas is preferably used as the oxidising agent.

9. A method as claimed in one of claims 1 to 8, characterised in that activated carbon is used as the adsorption agent.

10. A method as claimed in one of claims 1 to 9, characterised in that after bringing it into contact with a solution containing an oxidising agent, the adsorption agent is separated and recirculated.


1
Combustion device
2
Denitrogenation device (DeNO$_x$)
3
Dust removing device (E-Filter)
4
Active carbon particles
Desulphurisation device (EGD-device)
Combustion exhaust gases
5
Gypsum cylcone
Gypsum
Waste water cyclone
6
Waste Water
Suspension (*inter alia* adsorption agent)
Oxidising agent
Conversion with oxidising agent
Separation *inter alia* adsorption agent
Solid materials (*inter alia* adsorption agent)
Combustion
Precipitating agent
Conversion with precipitating agent
Separation of solid materials
Waste Water
Solid materials (*inter alia* Hg compounds)
Landfill