

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 613 397 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: 05.07.95 (51) Int. Cl.⁶: **B01D 53/34**, B01D 53/50,
B01D 53/64
- (21) Application number: **92923706.3**
- (22) Date of filing: **03.11.92**
- (96) International application number:
PCT/DK92/00318
- (97) International publication number:
WO 93/08902 (13.05.93 93/12)

(54) **A METHOD OF IMPROVING THE Hg-REMOVING CAPABILITY OF A FLUE GAS CLEANING PROCESS.**

(30) Priority: **04.11.91 US 787433**(43) Date of publication of application:
07.09.94 Bulletin 94/36(45) Publication of the grant of the patent:
05.07.95 Bulletin 95/27(84) Designated Contracting States:
AT DE DK GB IT

(56) References cited:

EP-A- 0 001 456	EP-A- 0 253 563
EP-A- 0 254 697	EP-A- 0 405 565
FR-A- 2 126 361	GB-A- 1 336 084
US-A- 4 619 608	

16TH ANNUAL CONFERENCE OF IEEE INDUSTRIAL ELECTRONICS SOCIETY vol. 1, November 1990, PACIFIC GROVE, CALIFORNIA
pages 396 - 401, XP000217028 S.
FUJII 'Modified linear predictor for Hg removal process of refuse incineration plants'

(73) Proprietor: **NIRO A/S**
Gladsaxevej 305
DK-2860 Soeborg (DK)

(72) Inventor: **FELSVANG, Karsten, Stig**
7238 Single Wheel Path
Columbia, MD 21046 (US)
Inventor: **NIELSEN, Kirsten, Kragh**
Ornebakken 50
DK-2840 Holte (DK)
Inventor: **CHRISTIANSEN, Ove, Brokner**
9816 Middle Meadow Road
Ellicott City, MD 21043 (US)

(74) Representative: **Simonsen, Christian Rosen-**
dal et al
c/o International Patent-Bureau
Hoeje Taastrup Boulevard 23
DK-2630 Taastrup (DK)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

Field of the invention.

5 The present invention relates in general to flue gas purification and more specific to the removal of noxious mercury vapor or compounds from flue gases originating from the combustion of coal, especially from flue gases from coal fired power plants.

Background of the invention and prior art.

10

In the field of municipal waste incineration it has within the last decades been realised that the flue gas resulting from the incineration must be purified to reduce the amount of noxious components therein.

Mercury is one of the noxious incinerator flue gas components the amount of which it is regarded as essential to reduce, and several measures have been suggested to this effect.

15

Thus, US patent specification 4,273,747 (Rasmussen) discloses reduction of the mercury content in hot incinerator flue gases by quenching said gases by atomizing an aqueous liquid therein in the presence of fly ash suspended in the gas, which quenching causes a cooling from a temperature of at least 200 °C to a temperature below 160 °C. The aqueous liquid may be water or an aqueous solution or suspension of an alkaline compound. This method will obviously not be suitable for flue gas from combustion of coal in power plants since the temperature of said gas is substantially below 200 °C, typically between 120 and 160 °C. Besides, the chemical composition of the major impurities of incinerator flue gas and power plant flue gas are so different that the mercury sorption will be influenced thereby.

20

European patent application no. 0013567 (Svenska Fläktfabriken) also deals with a process for reducing the mercury content of incinerator flue gas in which the gas is contacted with a solid sorbent consisting of powdered calcium hydroxide and of reaction products from the reaction between calcium hydroxide and gaseous hydrogen chloride. The specific conditions for obtainment of an efficient mercury removal are not disclosed but an efficient mercury removal is described in an example in which an incinerator flue gas is treated apparently having hydrogen chloride as the main pollutant.

25

In European patent no. 0 253 563 a method for removal of mercury and other noxious compounds from incinerator flue gas is disclosed in which an aqueous liquid containing a basic absorbent is atomized into the flue gas to absorb acidic components from the flue gas and simultaneously to evaporate the water in said aqueous liquid, in which process powdery activated carbon is injected into the flue gas and separated again from said gas together with particulate material formed as a result of chemical reactions and drying of the atomized basic absorbent.

30

A. S. Stepanov et al. in Prom. Sanit. Ochistka Gazov, 1979 (5)10, abstracted in Chemical Abstracts 92:168288y describe removal of mercury from gas by filtering through a layer of granulated activated charcoal modified by HCl.

35

European patent no. 0 254 697 describes a method for separating mercury from a water vapor containing gas in which the gas is contacted with a washing liquid in two or several stages in which process the gases are cooled to condense the water vapor in the gas and the gas is washed with a washing liquid containing hydrogen chloride and having a pH of about 3 or below to prevent sulphur dioxide to be dissolved in the washing liquid and to ensure that sufficient halide is present to form a complex compound with mercury. The specification of said European patent application teaches that it is essential that the pH of the washing liquid is so low that no substantial amount of SO₂ from the gas is dissolved in the washing liquid to form SO₃²⁻ since sulfite would reduce Hg²⁺ to Hg⁰, which would evaporate and thereby be re-emitted to the waste gas. Thus, the teaching of this European application is that chloride containing washing liquid for mercury removal must be acidic.

45

Also US patent no. 3,838,190 suggests to remove mercury from gases by means of acidic washing liquids. The washing liquids are sulphuric acid of a concentration of at least 50% containing chlorine and/or hydrogen chloride. The process is described as being suitable for gases arising by the combustion or roasting of sulphide containing ores or gases from electrolysis vessels. Obviously, the process is not suitable for flue gases from power plants.

50

US patent no. 4,729,882 deals with a process for removing mercury from gaseous emissions in which a chlorine containing material is added to the gaseous emissions and the mixture is heated to convert the mercury into mercuric chloride which are removed by scrubbing with wash water and fixed as HgCl₄²⁻. The process is described as being suitable for cleaning municipal refuse incinerator emissions. However, when scrubbing of the gas is made by an aqueous solution containing NaCl as Hg binding agent the Hg-removal is substantially below what is achieved by using certain metal complexing agents. The process is a wet

55

scrubbing process thereby having substantial disadvantages when compared with dry or semidry gas purification processes.

Moreover, it should be observed that it is well known to increase the adsorptive effect of activated carbon towards mercury vapor by impregnating the carbon with halogen or inter-halogen compounds as disclosed in US patent no. 3,662,523. The process of said US patent, however, involves passing the gas through a fixed bed of impregnated carbon. As described in the above mentioned European patent no. 0,253,563 such types of processes are less suited for flue gas treatment.

A discussion of the efficiency of Hg-removal by conventional flue gas purification systems, especially desulfurization methods may be found in a paper by Irene M. Smith: "Trace elements from coal combustion: emissions", IEA Coal Research, London, 1987, pages 54-65. It appears from said paper that in spite of the various systems described above for removing trace elements, especially mercury, from incinerator flue gases, the problem of such removal from coal-fired power plants waste gas still exists.

EP-A-0405565 shows a method of removing SO₂ and Hg from a gas containing these pollutants. The pollutants are removed by a two step washing process with an acetic washing liquid.

The flue gas from coal fired power plants differs from the flue gas from municipal incinerator plants in various aspects, especially the pollutants are diluted into a much larger proportion of flue gas; the temperature of said flue gas is lower and the chemical composition of the two types of gases are different.

Thus, the dominating pollutant in incinerator flue gases is often HCl whereas the primary pollutant in gases from coal combustion is SO₂.

Whereas the concern as to Hg pollution of the atmosphere has primarily resulted in the development of various systems for Hg-removal from incinerator flue gas it has within the last couple of years been realized that also the Hg-emissions from power plants etc. represent a substantial risk to the environment.

Since flue gas from coal combustion contains so much sulphur dioxide that a desulphurisation process of the flue gas is necessary, a process for reducing the Hg-content of coal combustion flue gas should preferably be compatible with or preferably incorporated into a gas desulphurisation process.

It has, however, turned out that if the processes used or suggested for incinerator flue gas cleaning in connection with or combined with desulphurisation processes, are transferred or modified to be used on coal combustion flue gas the results are more or less unpredictable and unreliable as far as Hg removal is concerned, as is further illustrated below.

Summary of the invention

We have now found that the Hg-removing capability of a flue gas cleaning process for flue gas having a temperature of 110-170°C, typically 120-160°C, and resulting from the combustion of coal having a low chloride content, in which process an aqueous suspension of a basic absorbent in a drying chamber of a drying absorption zone comprising a drying chamber and a particle collector as well as a duct connecting them, is atomized to fine droplets into the hot flue gas whereby the water of said droplets evaporates leaving dry fine particles and simultaneously a part of noxious components of the gas, including sulphur oxides, hydrogen halides and nitrogen oxides and mercury, are sorbed by the droplets of the fine particles, whereupon the flue gas with entrained dry fine particles is passed through the particle collector wherein contact between the particles and the flue gas causes a further sorption of noxious components, may be improved by increasing the amount of chloride supplied to the drying-absorption zone.

In the present specification and the attached claims the term "an aqueous suspension of a basic absorbent" is intended to cover also an aqueous solution of a basic absorbent in case the absorbent is highly water soluble, such as sodium carbonate.

In the present specification and the attached claims Hg or the word mercury means said element either as vapor of the metal or as a chemical compound or complex. The term "chloride" is intended to mean chloride ions as such or gaseous hydrogen chloride or compounds which by heating in the presence of coal forms Cl⁻ or HCl.

The chloride content of flue gases from coal combustion depends on the chloride content of the coal. Since said chloride content of coal mined at different locations varies substantially also the chloride content of the flue gas varies. By increasing the amount of chloride supplied to the drying-absorption zone in accordance with the method of the present invention it is possible with any quality of coal to achieve a high Hg-removing effect of the purification process in which primarily a desulphurisation is performed.

It has been experienced that the increase of the Hg-removing effect of chloride addition to the drying-absorption zone in a process treating flue gases of low chloride content is especially remarkable when activated carbon is present, but even without presence of carbon the effect is significant.

Activated carbon will often be present together with fly ash in the flue gas to be purified due to insufficient combustion, but in a preferred embodiment of the process powdery activated carbon is dispersed into the flue gas at a location upstream of the drying chamber into said chamber or downstream of the chamber but upstream of the particle collector.

5 The term activated carbon is here used in the broad sense comprising any carbonaceous material having sorbing activity and is thus not restricted to cover materials having been subjected to an activating treatment.

The powdery activated carbon is preferably used in an amount of 1-100 mg/Nm³ flue gas. Nm³ means the amount of gas having a volume of 1 m³ at atmospheric pressure and a temperature of 20°C.
10 Introduction of the powdery activated carbon into the process may be performed as described in European patent specification no. 0 253 563.

By the process according to the present invention various measures may be used for increasing the amount of chloride in the drying-absorption zone. Thus, said increase may conveniently be achieved by incorporating an alkaline- or alkaline earth metal salt or a solution thereof in the aqueous suspension of
15 basic absorbent. This may be achieved by substituting sea water partially or completely for water of low chloride content otherwise used for preparing the aqueous suspension of basic absorbent.

Such an increase of the chloride content of the absorbent suspension may further result in an increased desulphurisation efficiency of the process when lime or limestone is used as absorbent.

As supplement to or as alternative to incorporating chloride in the aqueous suspension of basic
20 absorbent, the increase of chloride in the drying-absorption zone may be achieved by increasing the chloride concentration of the flue gas by supplying a chloride or chlorine containing material to the coal before or during the combustion thereof and/or by injecting gaseous HCl into the flue gas upstream of or in the drying-absorption zone. When HCl is injected into the drying-absorption zone this may take place in the drying chamber or in the duct between the said chamber and the particle collector.

25 When HCl is injected upstream of the drying absorption zone this may take place in the combustion zone or at a site between said two zones.

Since most chloride or chlorine containing compounds will release gaseous chlorides when introduced into the combustion zone of a coal fired boiler several materials come into consideration for increasing the chloride content of the flue gas, however, for economic and operational reasons it is preferred to use
30 sodium or calcium chloride or chlorine containing waste plastic for said purpose.

When the process according to the invention is performed by increasing the chloride content of flue gas, the total chloride content of the flue gas, calculated as Cl⁻ is increased to at the most 150 ppm on weight basis.

A positive effect of the increase may, however, be obtained at total chloride concentrations substantially
35 lower dependent on operational conditions, equipment, presence of carbon in the flue gas etc. and a positive effect of chloride additions as low as 1 ppm is expected, especially when a simultaneous injection of activated carbon is made. The preferred total chloride concentration is 20-120 ppm, calculated as Cl⁻.

When the increase of chloride in the drying-absorption zone is obtained by adding chloride to the absorbent suspension such chloride is usually added in an amount to obtain a chloride concentration in
40 aqueous suspension between 0.1 and 8 percent by weight based on dry solids.

Detailed description of the invention.

Preferred embodiments of the invention is further described below with reference to the drawing
45 depicting a layout suitable for performing certain of said preferred embodiments.

The main elements shown on the Drawing are the drying chamber 1 and the particle collector 2 mutually connected by a duct 3. These three elements together constitute what in the present specification and in the attached claims is termed the drying-absorption zone.

A stream of flue gas from the preheater of a coal-fired boiler (not shown) is introduced into the drying
50 chamber 1 via a duct 4, optionally after having passed a dust collector (not shown).

An aqueous absorbent suspension is prepared in a mixing vessel 5 and by means of an atomizer wheel 6 atomized into the chamber 1. This absorbent suspension may be prepared for instance from slaked lime and recycled materials as described in US patent no. 4,279,873.

By contact with the hot flue gases in the chamber the water evaporates from the atomized suspension
55 whereby the temperature of the gas decreases substantially and at the same time acidic substances, mainly SO₂, in the flue gas react with the basic absorbent producing a particulate material primarily comprising salts formed by said reaction, together with non-reacted absorbent.

A part of this particulate material and of possible fly ash are recovered from the bottom of the spray absorption chamber through 7, whereas the remaining part of the particulate material is carried, entrained in the gas, through duct 3 into the particle collector 2.

The particle collector 2 may be a baghouse or an electrostatic precipitator in which substantially all particulate material is removed from the gas and recovered through 8.

From the particle collector 2 the thus cleaned gas may be conducted through a duct 9 to a stack 10 for release into the atmosphere.

The particulate material recovered through 7 and 8 may be partially recycled for preparing the absorbent suspension in the vessel 5 as explained above.

The process as described so far serves primarily to remove acidic components which in power plant flue gas essentially are sulphur oxides. However, also a certain part of Hg present in the flue gas will be removed together with the particulate material recovered through 7 and 8.

It has, however, turned out that the amount of Hg removed together with particulate material is far less than desired if the chloride content of the gas is low.

Therefore, a device 11 for measuring the chloride concentration in the flue gas may be inserted in the duct 4, or alternatively the chloride concentration in the flue gas is calculated or estimated on basis of the chloride contents of the coal used in the boiler.

If the chloride content is found to be below a certain value as defined above and in the attached claims arrangements are taken according to the invention for increasing the gas chloride content. This may be done in connection with an introduction of activated carbon which in itself also has a Hg removing effect and together with chloride addition exhibits a synergistic effect enabling an extremely efficient Hg removal.

In the embodiment shown, an apparatus 12 for dosing and injecting activated carbon is connected to the flue gas duct 4 through a conduit 14.

Before debouching into duct 4 the conduit 14 receives hydrogen chloride through conduit 15 connected to a HCl source 16.

Thus, hydrogen chloride and activated carbon are together introduced into the flue gas and, admixed with the latter, introduced into the spray drying absorption zone in 1, 3 and 2 thereby substantially increasing the Hg sorption taking place in this zone.

As indicated by means of the dotted lines the mixture of activated carbon and hydrogen chloride may be introduced directly into the drying chamber 1 or into the duct 3 as alternative to or as supplement to the introduction into the duct 4.

As explained above the chloride introduction may alternatively be performed separately from the introduction of activated carbon or it may be performed without using activated carbon. Especially, if the gas introduced through 4 contains carbon resulting from an incomplete combustion in the boiler.

As a further alternative to the above described embodiments or as a supplement thereto a chloride salt may be added to the absorbent suspension in the vessel 5 as indicated by 17 to obtain a mercury absorption improving increase of the chloride contents in the droplets of absorbent suspension atomized by the atomizer 6.

The amount of chloride introduced through 15 or 17 as well as the amount of activated carbon possibly dosed by means of 12 may be adjusted also on basis of the Hg content of the treated gas measured by means of a device 18 arranged in the duct 9.

The invention is further illustrated by means of the following examples and comparison examples.

Comparison Example 1

In a dry flue gas desulphurization system as the one illustrated on the drawing in which the particle collector 2 was a baghouse having fabric filter flue gas from a coal fired boiler was desulphurized. The plant was operated at full load corresponding to approx. 1.2×10^6 Nm³/h.

The amount of fly ash introduced through conduit 4 was approx. 10g/Nm³ and the flue gas temperature in 4 was 313 °F (156 °C) and the baghouse outlet temperature in duct 9 was 199 °F (93 °C).

Mercury was measured in and out of the system which means in duct 4 and in duct 9. No chloride was present in the flue gas or in the absorbent suspension prepared in vessel 5 and no chloride or activated carbon was added through conduit 14.

The following results were achieved:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
7.4	6.5	12
9.2	8.6	7
8.7	8.6	1

As it appears only approx. 7% average Hg removal was achieved in this process.

Comparison Example 2

A flue gas desulphurization system as shown on the drawing wherein the particle collector 2 was an electrostatic precipitator was used to desulphurize flue gas from a coal fired boiler. The plant was operating at full load corresponding to approx. $1.8 \times 10^6 \text{ Nm}^3/\text{h}$.

The fly ash introduced together with the flue gas was in the order of $10 \text{ g}/\text{Nm}^3$.

Flue gas inlet temperature in duct 4 was 305°F (152°C) and the electrostatic precipitator outlet temperature in duct 9 was 160°F (87°C).

No chloride was present in the flue gas or in the absorption suspension prepared in vessel 5.

Mercury was measured in and out of the system and the following results achieved:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
5.6	4.7	16
3.8	2.4	37
3.8	2.8	26
3.9	3.3	15

An average mercury removal of 24% was obtained with this system.

Comparison Example 3

A flue gas desulphurization system of the type shown on the drawing in which the particle collector was a bag house was used to desulphurize flue gas from a coal fired boiler.

The plant was operated at full load corresponding to approx. $2.2 \times 10^6 \text{ Nm}^3/\text{h}$.

Fly ash in the gas to be treated was in the order of $10 \text{ g}/\text{Nm}^3$.

The flue gas inlet temperature in duct 4 was 306°F (152°C) and baghouse outlet temperature 175°F (79°C).

No chloride was present in the flue gas or in the absorption suspension.

Mercury was measured in the gas at the inlet and the outlet of the system and the following results were achieved:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
11	8.9	19
11	9.1	17
9.9	9.2	7
11	9.3	15

An average of 15% Hg removal was obtained with this system.

Example 1

This Example was performed as Comparison Example 2 above apart from the fact that calcium chloride was added to the absorbent suspension produced in vessel 5. The calcium chloride was added in an amount corresponding to 2.5 percent by weight Cl in the absorbent suspension, based on dry solids.

Mercury was measured in and out of the system and the following results were obtained:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
3.9	0.80	80
3.7	0.95	74

An average mercury removal of 77% was obtained with this system, which means a substantial improvement over the Hg absorption experienced in Comparison Example 2.

In the following examples the HCl content of the flue gas originated from chloride present in or added to the coal.

Example 2

A dry flue gas desulphurization system as the one depicted on the drawing but supplemented with an electrostatic precipitator upstream of duct 4 for fly ash collection, and in which the particle collector 2 was a baghouse was used desulphurize flue gas from a coal fired boiler.

The plant was operated at full load corresponding to $1.2 \times 10^6 \text{ Nm}^3/\text{h}$.

The fly ash in the flue gas introduced through duct 4 was in the order of $50 \text{ mg}/\text{Nm}^3$. The temperature of the gas in duct 4 was 275°F (135°C) and baghouse outlet temperature 158°F (70°C).

HCl concentration in the flue gas introduced through duct 4 was $90 \text{ mg}/\text{Nm}^3$.

Mercury was measured in and out of the system and the following results were achieved:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
2.9	1.3	56

Example 3

A dry flue gas desulphurization system as shown on the drawing was used. As in Example 2 the system was supplemented with an electrostatic precipitator for fly ash collection upstream of duct 4. The particle collector 2 was an electrostatic precipitator.

The plant was used to desulphurize flue gas from a coal fired boiler. The plant was operated at full load corresponding to approx. $1.1 \times 10^6 \text{ Nm}^3/\text{h}$. The amount of fly ash introduced by the flue gas through duct 4 was in the order of $1.2 \text{ g}/\text{Nm}^3$. Gas temperature in duct 4 was 257°F (125°C) and the outlet temperature in duct 9 was 158°F (70°C).

HCl concentration in the flue gas was approx. $65 \text{ mg}/\text{Nm}^3$.

Mercury was measured in and out of the system and the following results obtained:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
2.74	0.32	88
2.61	0.29	89

89% removal was obtained with this system.

Example 4

A dry flue gas desulphurization system consisting of a plant as the one shown on the drawing wherein the particle collector 2 is a baghouse, was used to treat flue gas from a coal fired boiler.

The plant was operated at full load corresponding to $0.11 \times 10^6 \text{ Nm}^3/\text{h}$ and fly ash in the flue gas in duct 4 was in the order of $10 \text{ g}/\text{Nm}^3$.

The temperature of the gas in duct 4 was 342°F (172°C) and outlet temperature from the baghouse was 175°F (79°C).

HCl concentration in the flue gas was $142 \text{ mg}/\text{Nm}^3$.

Mercury was measured in and out of the system. The following results were achieved:

Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
5.4	0.14	97
5.2	0.18	97
5.0	0.20	96
4.7	0.18	96

Average removal with this system is 96%.

The above process was modified by adding activated carbon through conduit 14 to the stream of flue gas in duct 4 upstream of the drying chamber. Mercury was measured in and out of the system.

The following results were achieved:

Amount of carbon mg/Nm^3	Inlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	Outlet $\mu\text{gHg}/\text{Nm}^3$ at 5% O_2	% Removal
8	4.0	0.10	98
8	4.4	<0.01	>99.8
36	6.2	0.01	99.8
36	5.6	<0.01	>99.7

Average removal with addition of activated carbon was thus better than 99%.

Claims

1. A method for removing noxious components including sulphur dioxide and mercury from a hot flue gas having a temperature of 110-170°C and resulting from the combustion of coal having a low chloride content, in which process an aqueous suspension of a basic absorbent in a drying chamber of a drying-absorption zone comprising a drying chamber and a particle collector as well as a duct connecting them, is atomized to fine droplets into the hot flue gas, the water of said droplets evaporates leaving dry fine particles, and a part of noxious components of the gas including sulphur oxides, hydrogen halides and nitrogen oxides and mercury, is simultaneously sorbed by the droplets and the fine particles, whereupon the flue gas with entrained dry fine particles is passed to the particle collector wherein contact between the particles and the flue gas causes a further sorption of noxious compounds, in which the amount of chloride supplied to the drying-absorption zone is increased to an extent sufficient to improve the Hg sequestering capability of the process.
2. The method of claim 1, wherein the increase of the amount of chloride in the drying-absorption zone is accomplished by increasing the chloride concentration in the flue gas by one or both of the following measures (a) adding a chloride or chlorine containing material to the coal before or during the combustion thereof, and (b) injecting gaseous HCl into the flue gas upstream of or into the drying-absorption zone.
3. The method of claim 1, wherein the increase of the amount of chloride in the drying absorption zone is accomplished by incorporating an alkaline metal or alkaline earth metal salt or a solution thereof in the aqueous suspension of basic absorbent.
4. The method of claim 1-3, wherein powdery activated carbon is dispersed into the flue gas at a location upstream of, into or downstream of the drying chamber but upstream of the particle collector.
5. The method of claim 4, wherein the activated carbon is used in an amount of 1-100 mg/Nm^3 flue gas.
6. The method of claim 4, wherein 90-99% of the Hg content of the flue gas is removed by increasing the chloride content of the gas supplied to the drying-absorption zone to 20-150 ppm and by dispersing activated carbon into the flue gas in an amount of 1-100 mg/Nm^3 .

7. The method of any of the claims 1-6, wherein said increase of the chloride supply is made in response to the result of Hg analysis of the flue gas leaving the particle collector.
8. The method of any of the claims 1-6, wherein said increase of the chloride supply is made in dependency of the chloride content of the flue gas entering the drying-absorption zone.
9. The method of claim 8, wherein said chloride content is measured by gas analysis and/or estimated by calculations based on chloride analysis of the coal.
10. The method of claim 2, wherein a chloride or chlorine containing material is added to the coal before or during combustion thereof in an amount sufficient to obtain a total chloride concentration in the flue gas of at least 1 ppm by weight.
11. The method of any of the preceding claims wherein a total chloride concentration in the flue gas of 20-120 ppm is obtained.

Patentansprüche

1. Verfahren zur Entfernung schädlicher Bestandteile einschliesslich Schwefeldioxyd und Quecksilber aus einem von Kohlenverbrennung stammenden heissen Abgas mit einer Temperatur von 110-170 °C und einem niedrigen Chlorid-Inhalt, bei welchem Verfahren eine wässrige Lösung eines basischen Absorptionsmittels in einer Trockenkammer einer Trocknungs-Absorptions-Zone umfassend eine Trockenkammer und einen Partikelsammler sowie einen diese verbindenden Kanal, in feine Tropfen in das heisse Abgas zerstäubt wird, wobei das Wasser dieser Tropfen verdampft und trockene feine Partikeln hinterlässt, und ein Teil der schädlichen Bestandteile des Gases umfassend Schwefeloxye, Wasserstoffhalogenide und Stickstoffoxyde und Quecksilber durch die Tropfen und die feinen Partikeln gleichzeitig sorbiert wird, wonach das Abgas mit mitgeführten feinen Partikeln zum Partikelsammler geleitet wird, wo Kontakt zwischen den Partikeln und dem Abgas zu einer zusätzlichen Sorption von schädlichen Bestandteilen führt, worin die Menge des der Trocknungs-Absorptions-Zone zugeführten Chlorids auf ein Ausmass erhöht wird, die zur Verbesserung der Hg-Entfernungskapazität des Verfahrens ausreichend ist.
2. Verfahren nach Anspruch 1, bei welchem die Erhöhung der Chloridmenge in der Trocknungs-Absorptions-Zone durch ein Erhöhen der Chlorid-Konzentration im Abgas in einem oder beiden der folgenden Massnahmen: (a) Zugabe eines Chlorids oder Chlorid-haltigen Materials zur Kohle vor oder unter deren Verbrennung, und (b) Einspritzen von gasförmigem HCl in das Abgas stromaufwärts der Trocknungs-Absorptionszone oder in diese, stattfindet.
3. Verfahren nach Anspruch 1, bei welchem die Erhöhung der Chloridmenge in der Trocknungs-Absorptions-Zone durch Aufnahme eines Alkalimetall- oder eines Erdalkalimetallsalzes oder dessen Lösung in die wässrige Suspension eines basischen Absorptionsmittels vollendet wird.
4. Verfahren nach Anspruch 1-3, bei welchem pulverförmige aktive Kohle an einer Stelle stromaufwärts der Trockenkammer, in die Trockenkammer oder stromabwärts davon, aber stromaufwärts des Partikelsammlers in das Abgas dispergiert wird.
5. Verfahren nach Anspruch 4, nach welchem die aktive Kohle in einer Menge von 1-100 mg/Nm³ Abgas benutzt wird.
6. Verfahren nach Anspruch 4, bei welchem durch Erhöhung des Chlorid-Inhalts des zu der Trocknungs-Absorptions-Zone geleiteten Gases auf 20-150 ppm und Dispersion von aktiver Kohle in einer Menge von 1-100 mg/Nm³ in das Abgas 90-99% des Hg-Inhalts im Abgas beseitigt wird.
7. Verfahren nach einem der Ansprüche 1-6, wobei die Erhöhung der Chloridzugabe auf Grundlage des Ergebnisses von Hg-Analysen des den Partikelsammler verlassenden Gases erfolgt.
8. Verfahren nach einem der Ansprüche 1-6, wobei die Erhöhung der Chloridzugabe vom Chloridgehalt des in die Trocknungs-Absorptions-Zone einströmenden Gases abhängt.

9. Verfahren nach Anspruch 8, bei welchem der Chlorid-inhalt in Gasanalysen berechnet und/oder auf Basis von Chlorid-Analysen der Kohle durchgeführten Berechnungen geschätzt wird.
10. Verfahren nach Anspruch 2, bei welchem ein Chlorid-oder Chlor-haltiges Material der Kohle vor oder unter deren Verbrennung in einer Menge zugefügt wird, die zum Erhalt einer totalen Chlorid-Konzentration von mindestens 1 Gew.-ppm im Abgas ausreichend ist.
11. Verfahren nach einem der vorhergehenden Ansprüche, nach welchem eine totale Chlorid-Konzentration von 20-120 ppm im Abgas erreicht wird.

Revendications

1. Procédé d'élimination de composants nocifs comprenant de l'anhydride sulfureux et du mercure, de gaz effluents chauds présentant une température de 110 à 170 °C et provenant de la combustion de charbon à faible taux de chlorure, procédé dans lequel une suspension aqueuse d'un absorbant basique, dans une chambre de séchage d'une zone de séchage-absorption comprenant une chambre de séchage et un collecteur de particules ainsi qu'une conduite les reliant, est atomisée en fines gouttelettes dans les gaz effluents chauds, l'eau desdites gouttelettes se trouvant ainsi évaporée et laissant des fines particules sèches, et dans lequel une partie des composants nocifs des gaz, comprenant oxydes de soufre, halogènes hydrogénés, oxydes d'azote et mercure, est simultanément absorbée par les gouttelettes et les fines particules, après quoi les gaz effluents et les fines particules sèches entraînées sont transférés au collecteur de particules dans lequel le contact entre les particules et les gaz effluents provoque une absorption supplémentaire des composants nocifs, la quantité de chlorure fournie à la zone de séchage-absorption étant accrue à un degré suffisant pour améliorer l'aptitude du procédé à retenir Hg.
2. Procédé selon la revendication 1, dans lequel l'accroissement de la quantité de chlorure dans la zone de séchage-absorption est effectué par augmentation de la concentration de chlorure dans les gaz effluents, suivant l'une des deux ou les deux mesures suivantes: (a) addition de chlorure ou de matériau contenant du chlore dans le charbon, avant ou durant la combustion de celui-ci, et (b) injection de HCl gazeux dans l'effluent, en amont de ou dans la zone de séchage-absorption.
3. Procédé selon la revendication 1, dans lequel l'accroissement de la quantité de chlorure dans la zone de séchage-absorption est effectué par adjonction d'un métal alcalin ou de sel de métal alcalino-terreux ou d'une solution de ceux-ci dans la suspension aqueuse de l'absorbant basique.
4. Procédé selon les revendications 1 à 3, dans lequel de la poudre de carbone activé est dispersée dans l'effluent gazeux en un emplacement situé en amont de, dans ou en aval de la chambre de séchage, mais en amont du collecteur de particules.
5. Procédé selon la revendication 4, selon lequel le carbone activé est utilisé en une quantité de 1 à 100 mg par Nm³ d'effluent gazeux.
6. Procédé selon la revendication 4, dans lequel 90 à 99% du contenu de Hg dans le gaz effluent sont éliminés par accroissement de la quantité de chlorure dans le gaz alimentant la zone de séchage-absorption jusqu'à 20 à 150 ppm et par dispersion, dans le gaz effluent, de carbone activé en une quantité de 1 à 100 mg/Nm³.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ledit accroissement d'alimentation en chlorure est effectué en fonction du résultat de l'analyse de Hg du gaz effluent quittant le collecteur de particules.
8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel ledit accroissement d'alimentation en chlorure est effectué en fonction du contenu de chlorure dans le gaz effluent entrant dans la zone de séchage-absorption.
9. Procédé selon la revendication 8, dans lequel ledit contenu en chlorure est mesuré par analyse de gaz et/ou estimé par calculs basés sur l'analyse de chlorure dans le charbon.

10. Procédé selon la revendication 2, dans lequel un chlorure ou un matériau contenant du chlore est ajouté au charbon avant ou durant la combustion de celui-ci, en quantité suffisante pour obtenir, dans le gaz effluent, une concentration totale en chlorure d'au moins 1 ppm en poids.
- 5 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel on obtient une concentration totale en chlorure dans le gaz effluent d'au moins 20 à 120 ppm.

10

15

20

25

30

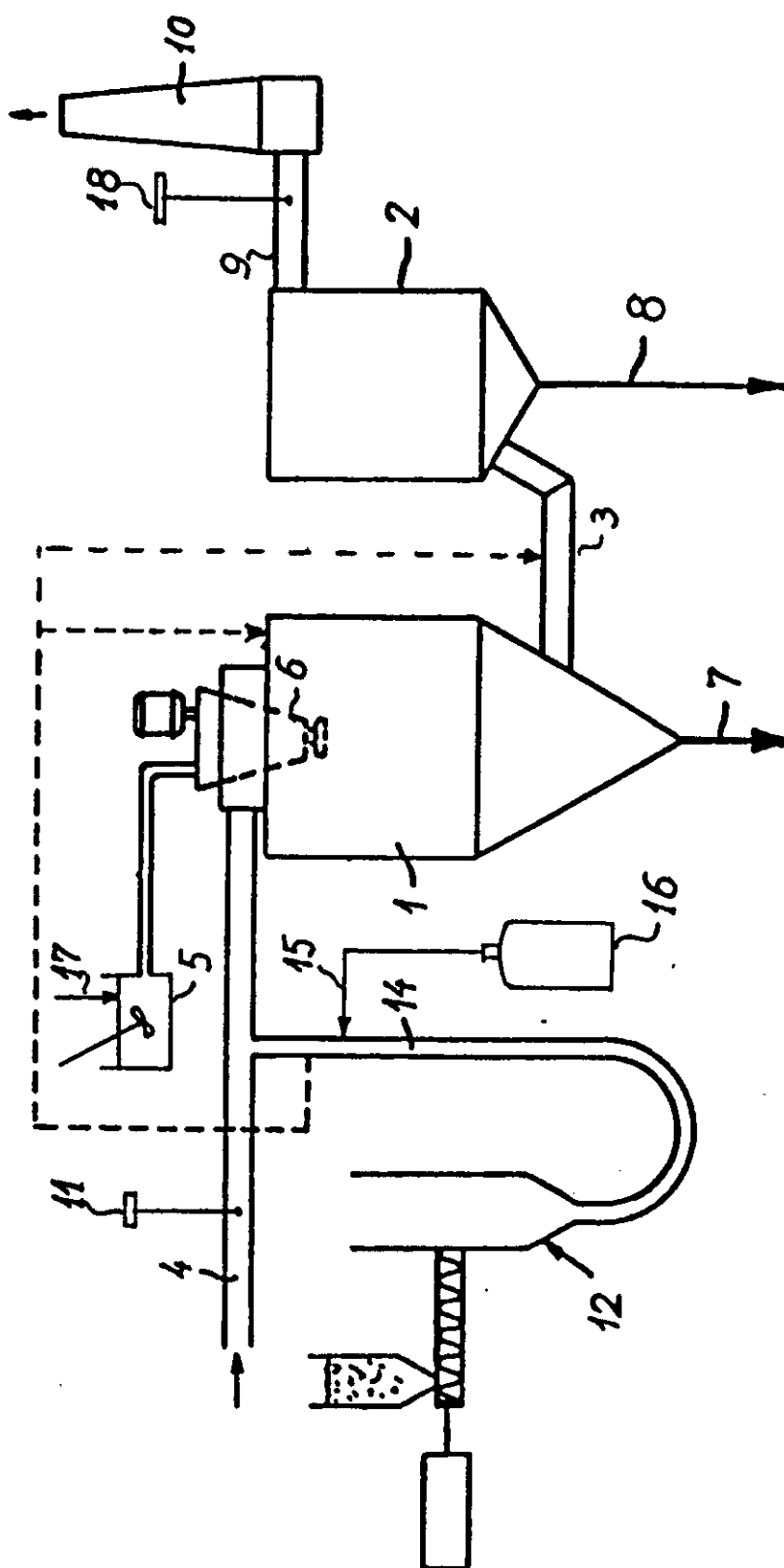
35

40

45

50

55



REGISTER ENTRY FOR EP0613397

European Application No EP92923706.3 filing date 03.11.1992

Priority claimed:

04.11.1991 in United States of America - doc: 787433

PCT EUROPEAN PHASE

PCT Application PCT/DK92/00318 Publication No WO93/08902 on 13.05.1993

Designated States DE DK GB IT AT

Title A METHOD OF IMPROVING THE HG-REMOVING CAPABILITY OF A FLUE GAS CLEANING PROCESS.

Applicant/Proprietor

NIRO A/S, Gladsaxevej 305, DK-2860 Soeborg, Denmark [ADP No. 58815317001]

Inventors

KARSTEN STIG FELSVANG, 7238 Single Wheel Path, Columbia, MD 21046, United States of America [ADP No. 62221791001]

KIRSTEN KRAGH NIELSEN, Ornebakken 50, DK-2840 Holte, Denmark [ADP No. 62221809001]

OVE BROKNER CHRISTIANSEN, 9816 Middle Meadow Road, Ellicott City, MD 21043, United States of America [ADP No. 62221817001]

Classified to

B01D

Address for Service

STEVENS, HEWLETT & PERKINS, 1 St Augustine's Place, BRISTOL, BS1 4UD, United Kingdom [ADP No. 00001545002]

EPO Representative

CHRISTIAN ROSENDAL SIMONSEN, c/o Internationalt Patent-Bureau Hoeje Taastrup Boulevard 23, DK-2630 Taastrup, Denmark [ADP No. 57244956001]

Publication No EP0613397 dated 07.09.1994

Publication in English

Examination requested 15.04.1994

Patent Granted with effect from 05.07.1995 (Section 25(1)) with title A METHOD OF IMPROVING THE HG-REMOVING CAPABILITY OF A FLUE GAS CLEANING PROCESS.

**** END OF REGISTER ENTRY ****

OA80-01
EP

OPTICS - PATENTS

16/10/95

10:33:41
PAGE: 1

RENEWAL DETAILS

PUBLICATION NUMBER

EP0613397

PROPRIETOR(S)

NIRO A/S, Gladsaxevej 305, DK-2860 Soeborg, Denmark

DATE FILED

03.11.1992

DATE GRANTED

05.07.1995

DATE NEXT RENEWAL DUE

03.11.1996

DATE NOT IN FORCE

DATE OF LAST RENEWAL

YEAR OF LAST RENEWAL

00

STATUS

PATENT IN FORCE

**** END OF REPORT ****