

Description

Title: Method for treating flue gas from combustion units

Technical field

[1] This invention relates to reducing the acid gas concentration in flue gas
5 produced in a combustion unit, for example an incinerator for household refuse or
for industrial hazardous waste.

[2] Currently in France, incineration is the number two method of waste
disposal. This waste comes from household trash as well as from hazardous
industrial waste. Combustion of this waste results in the emission of flue gas
10 containing acid gases such as nitrogen oxides (NO_x), hydrochloric acid (HCl), and
sulfur dioxide (SO_2). Acid gases are pollutants that are harmful to humans as well
as to the environment; their maximum concentration in flue gas is therefore set by
regulatory standards. For example, according to the regulatory standard currently in
force (Directive 2000/76/EC) of 11% O_2 , the emission limit values are set at
15 200 mg/Nm^3 for NO_x (NO_2 equivalent), 10 mg/Nm^3 for HCl , and 50 mg/Nm^3 for SO_2 .

Prior art

[3] The reduction in the concentration of acid gases contained in combustion
flue gas is conventionally achieved by reacting said acid gases with one or more
neutralizing reagents. These neutralizing reagents are selected according to the
20 acid gases to be treated. For example, the NO_x concentration can be reduced by a
selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) in
the presence of neutralizing reagents such as ammonia (NH_3) or urea ($\text{CO}(\text{NH}_2)_2$).
SNCR is performed at high temperature (around 950°C), while SCR is performed at
low temperature (around 300°C). The HCl and SO_2 concentrations are
25 conventionally reduced by a process of forming chlorides and sulfates with
neutralizing reagents which can be lime, sodium bicarbonate, or soda.

[4] These processes are effective in routine practice but do not always allow
maintaining the concentrations of NO_x , SO_2 , and HCl below the limit values, in
particular when peaks of acid gas concentrations appear in the flue gas. To respond

to this problem, neutralizing reagents are injected in excess quantity, which leads to significant consumption of said neutralizing reagents. This significant consumption leads to a considerable added cost of raw materials and requires frequent maintenance shutdowns.

5 **[5]** The neutralizing reagents involved in these processes are also hazardous for the operators.

[6] In addition, these processes can generate corrosion and/or cause fouling of the boilers of the combustion units, which decreases the production of energy by said boilers.

10 **[7]** To solve this last problem, WO 2013/060991 describes a reagent capable of neutralizing SO₂/HCl acid gases directly in the combustion furnace or in the post-combustion chamber of a combustion unit. This reagent may comprise products based on alkalis, alkaline earth metals, calcium oxide, hydrated lime, limestone, calcium carboxylic salts, clays, and/or reducing organic compounds. This reagent therefore does not include ammonium salts. In addition, it is not intended to reduce
15 the concentration of acid gases other than SO₂ and HCl, for example NO_x.

Technical problem

[8] There is therefore always a need for an efficient, safe, and economical solution for decreasing the concentration of a wide range of acid gases contained in flue gas produced in a combustion unit, such as incinerators for household waste or
20 for industrial hazardous waste.

[9] It is thus to the credit of the inventors that they have found it possible to meet this need by means of a reactive powder composition comprising an alkaline earth salt and an ammonium salt.

Summary

25 **[10]** Thus, a first aspect of the present disclosure is a method for treating combustion flue gas comprising acid gases, said method comprising a contact step a) of placing said acid gases in contact with a powder composition comprising an alkaline earth metal

salt and an ammonium salt in an oxidizing atmosphere and at a temperature greater than or equal to 850°C, wherein the ammonium salt is selected among ammonium carbonate, ammonium chloride, ammonium sulfate, ammonium sulfide, and mixtures thereof, and wherein the powder composition comprises, relative to the
5 total weight of the composition, at least 50% of alkaline earth metal salt, and the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3.

[11] Advantageously, the method according to the present disclosure makes it possible to reduce the concentration of acid gases in combustion flue gas in an
10 efficient manner.

[12] The method according to the present disclosure thus advantageously makes it possible to maintain the concentration of acid gases in combustion flue gas below the values set by regulatory standards even when peaks in the acid gas concentration appear in the combustion flue gas.

15 **[13]** The method according to the present disclosure is also more economical and safer than conventional methods for reducing the acid gas concentration in combustion flue gas, because:

- the cost of the powder composition is lower than that of the neutralizing reagents conventionally used, and
- 20 - an efficient reduction of the acid gas concentration in combustion flue gas allows significantly reducing the consumption of the neutralizing reagents conventionally used, and therefore reducing the costs and risks associated with said neutralizing reagents and reducing the costly maintenance shutdowns.

25 **[14]** A second aspect of the present disclosure is a powder composition comprising an alkaline earth metal salt and an ammonium salt comprising, relative to the total weight of the composition, at least 50% of alkaline earth metal salt, and the mass ratio between the ammonium salt and the alkaline earth metal salt is from

0.05 to 0.3, and wherein the ammonium salt is selected among ammonium carbonate, ammonium chloride, ammonium sulfate, ammonium sulfide, and mixtures thereof.

Brief description of drawings

5 Fig. 1

[15] [Fig. 1] is a diagram illustrating a combustion unit.

Detailed description of the invention

[16] According to a first object, the invention relates to a method for treating combustion flue gas comprising acid gases, said method comprising a contact step
10 a) of placing said acid gases in contact with a powder composition comprising an alkaline earth metal salt and an ammonium salt in an oxidizing atmosphere and at

a temperature greater than or equal to 850°C, in particular at a temperature comprised between 900°C to 1000°C, more particularly 940°C to 960°C.

[17] For the purposes of the invention, the term "combustion flue gas" is understood to mean flue gas produced in a combustion unit. A combustion unit is conventionally an industrial facility intended for the incineration of waste, such as non-hazardous or hazardous waste, municipal or industrial sludge, but also for the combustion of biomass or coal or coal-biomass co-combustion.

[18] For the purposes of the invention, the term "powder composition" is understood to mean a composition in the form of powder. In particular, the maximum diameter of 90% of the particles in the volume distribution (d90) of the powder composition according to the invention can be less than or equal to 50 µm, preferably from 2 µm to 10 µm, more preferably from 4 µm to 6 µm. The d90 value is determined by liquid laser particle size distribution in distilled water with a Malvern-Mastersizer 2000 laser particle size analyzer equipped with a "small volume" cell of 120 ml; the signal is processed with Mie's mathematical model.

[19] Advantageously, a particle size distribution in the above ranges makes it possible to increase the contact surface area of the powder composition with the acid gases of the combustion flue gas and thus to increase the efficiency of the reduction in the acid gas concentration in combustion flue gas.

[20] For the purposes of the present invention, the term "alkaline earth metal salt" is understood to mean a chemical compound comprising an anion and an alkaline earth metal cation, such as a cation of beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radon (Ra), and mixtures thereof. Preferably, the alkaline earth metal salt is selected among a magnesium salt, a calcium salt, and mixtures thereof. More preferably, it is a calcium salt.

[21] For the purposes of the present invention, the term "ammonium salt" is intended to mean a chemical compound comprising an anion and an ammonium cation of the crude formula NH_4^+ .

[22] For the purposes of the present invention, the term "oxidizing atmosphere" is understood to mean an atmosphere comprising oxygen (O_2) and carbon dioxide

(CO₂). Typically, the partial pressure of O₂ (PO₂) in the oxidizing atmosphere is less than 0.5 bar, more particularly from 0.01 bar to 0.25 bar, even more particularly from 0.05 bar to 0.1 bar. Typically, the partial pressure of CO₂ (PCO₂) in the oxidizing atmosphere is less than 0.5 bar, more particularly from 0.05 bar to 0.2 bar, even
5 more particularly from 0.095 bar to 0.15 bar.

[23] Without wishing to be bound by any theory, the inventors are of the opinion that, during the contact step a), the alkaline earth metal and the ammonium salt respectively form an oxide of the alkaline earth metal and of ammonia (NH₃) which react with the acid gases of the combustion flue gas. By means of this reaction
10 sequence, the reduction in the concentration of acid gases in combustion flue gas by the powder composition is highly efficient.

[24] The chemical composition of acid gases depends on the composition of the waste to be incinerated. For the purposes of the present invention, the term "acid gas" is understood to mean a gas which, on contact with water, produces an
15 aqueous solution having an acidic pH, i.e. a pH less than 7. Typically, acid gases are classified according to the five following categories:

- phosphorous acid gases such as phosphoric acid (H₃PO₄),
- carbonaceous acid gases such as carbon dioxide (CO₂),
- nitrous acid gases such as nitrogen oxides (NO_x), hydrogen cyanide (HCN),
20 and mixtures thereof,
- sulfurous acid gases such as sulfur dioxide (SO₂), hydrogen sulfide (H₂S), and mixtures thereof, and
- halogenated acid gases such as hydrogen fluoride (HF), difluoride (F₂), hydrogen chloride (HCl), chlorine (Cl₂), hydrogen bromide (HBr), bromine
25 (Br₂), hydrogen iodide (HI), iodine (I₂), and mixtures thereof, in particular hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr), and mixtures thereof, and more particularly hydrogen chloride (HCl).

[25] According to one embodiment, the acid gases can be selected among H₃PO₄, CO₂, NO_x, HCN, SO₂, H₂S, HF, F₂, HCl, Cl₂, HBr, Br₂, HI, I₂, and mixtures
30 thereof, in particular selected among CO₂, NO_x, HCN, SO₂, H₂S, HF, HCl, HBr, and mixtures thereof.

[26] According to one specific embodiment, the acid gases can be selected among NO_x, SO₂, HCl, and mixtures thereof.

[27] This specific embodiment is very advantageous because the powder composition efficiently and all at once reduces the concentration of NO_x, SO₂, HCl, or mixtures thereof in said combustion flue gas. Indeed, during the contact step a) the ammonia reacts with NO_x to form nitrogen (N₂) and water (H₂O), and the alkaline earth metal oxide reacts with SO₂ by a sulfation reaction and with HCl by a chlorination reaction.

[28] In particular, the method according to the invention allows an efficient reduction of the SO₂ concentration. Indeed, the sulfation reaction is thermodynamically facilitated in the presence of HCl and under the operating conditions of the contact step a).

[29] Advantageously, the alkaline earth metal salt can comprise a cation selected among a magnesium cation, a calcium cation, and mixtures thereof, and preferably can be the calcium cation. Typically, the anion of the alkaline earth metal salt can be selected among an acetate, an acrylate, a carbonate, a formate, a propionate, and mixtures thereof, in particular among an acetate, an acrylate, a carbonate, and mixtures thereof; more particularly the anion is a carbonate.

[30] According to one specific embodiment, the alkaline earth metal salt is a calcium salt, in particular calcium carbonate.

[31] The calcium carbonate can come from chalk, limestone, lime, industrial waste, and mixtures thereof, in particular from lime, industrial waste, and a mixture thereof, more particularly from lime.

[32] For example, the industrial waste can be selected among mineral sludge, in particular mineral sludge mainly composed of calcium carbonate and which can, if necessary, be transformed into a powder reagent by means of one or more suitable chemical treatments. The chemical treatments are those known to those skilled in the art such as, for example, washing, drying, physicochemical treatments. Decarbonation sludge, sludge from primary brine purification, and a mixture thereof, are quite suitable for use in the invention.

[33] Decarbonation sludge is a non-hazardous waste conventionally generated during a water decarbonation operation, an operation implemented at industrial sites requiring supplies of softened water. Each of these sites can generate 1,000 to 3,000 tons/year of decarbonation sludge. Advantageously, using decarbonation
5 sludge as a source of calcium carbonate therefore makes it possible to monetize waste which is not currently monetized and to create a circular economy by the availability of this waste around the incinerators. This also makes it possible to replace a natural resource (chalk, limestone, and lime) with waste. Decarbonation sludge generally comprises about 65% calcium carbonate, the remainder being
10 water. To be used in step a) of the method of the invention, it can therefore be dried so that the calcium carbonate content in the dried sludge is between 94% and 99.6%.

[34] Sludge from primary brine purification is waste resulting from electrolysis in the production of chlorine. It contains calcium and magnesium carbonates as well as traces of pollutants, salts, and possibly metals. The pollutants, salts, and possible
15 metals can be separated by specific operations known to those skilled in the art, such as successive washings or physicochemical treatments. The water can be removed by drying.

[35] Advantageously, under the operating conditions of the contact step a), the kinetics of the oxidation of calcium salts to calcium oxide (CaO) and the kinetics of
20 the reaction between CaO and the acid gases are very fast. The reduction in the concentration of acid gases is then highly efficient. This is all the more true if the calcium salt is calcium carbonate and the acid gases comprise SO₂ and/or HCl.

[36] According to one embodiment, the ammonium salt can be selected among ammonium carbonate, ammonium chloride, ammonium sulfate, ammonium sulfide,
25 and mixtures thereof; in particular the ammonium salt is ammonium sulfate.

[37] Advantageously, under the operating conditions of the method according to the invention, the kinetics of the formation of ammonia from ammonium sulfate is rapid. The reduction in the concentration of acid gases is then highly efficient. This is all the more true if the acid gases comprise NO_x.

30 **[38]** Ammonium sulfate also exhibits an anti-fouling property. The fouling of combustion units is caused by the formation and deposition of ash during the

incineration of wastes comprising high concentrations of chlorine and alkaline substances. Fouling has a significant economic impact, because it affects the proper operation of the boiler of the combustion unit, which limits the production of energy by said boiler. In addition, if the fouling becomes too significant, it requires a
5 complete shutdown of the boiler for maintenance and thus of the combustion unit. Due to its anti-fouling property, ammonium sulfate advantageously maintains the proper operation and the energy performance of the boiler. Ammonium sulfate also increases the interval of time between two complete shutdowns for maintenance of the combustion unit.

10 **[39]** According to one embodiment, the powder composition may comprise, relative to the total weight of the composition, at least 50% of alkaline earth metal salt, in particular from 60% to 90% of alkaline earth metal salt, more particularly from 69% to 71% of alkaline earth metal salt, and the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3, in particular from 0.15 to
15 0.25, more particularly from 0.20 to 0.22.

[40] Advantageously, the powder composition of this embodiment allows an efficient reduction of the concentration of acid gases contained in combustion flue gas without altering the operation of the combustion unit.

[41] Indeed, when the mass percentage of the alkaline earth salt in the powder
20 composition and the mass ratio between the ammonium salt and the alkaline earth metal salt are lower than the values indicated above, then there can be a shortfall of ammonia and alkaline earth metal oxide relative to the acid gases such that the reduction in the acid gas concentration in the flue gas is less efficient.

[42] Similarly, when the mass ratio between the ammonium salt and the alkaline
25 earth metal salt is greater than the values indicated above, then there may be an excess of ammonia, which is a corrosive and toxic compound, relative to the acid gases. This excess ammonia can, for example, damage the combustion unit and require a specific treatment unit.

[43] According to one embodiment, the powder composition may comprise
30 calcium carbonate and ammonium sulfate.

[44] According to a variant of this embodiment, the powder composition may comprise, relative to the total weight of the composition, at least 50% of calcium carbonate, in particular from 60% to 90% of calcium carbonate, and the mass ratio between the ammonium sulfate and the calcium carbonate is from 0.05 to 0.3, in particular from 0.15 to 0.25.

[45] More particularly, the powder composition may comprise, relative to the total weight of the composition, from 69% to 71% of calcium carbonate, and the mass ratio between the ammonium sulfate and the calcium carbonate is from 0.20 to 0.22.

[46] According to one embodiment, the powder composition according to the invention may further comprise an additive. This additive can be selected among a clay, a bromine salt, and mixtures thereof; in particular the additive is a clay.

[47] For the purposes of the present invention, the term "clay" is understood to mean a chemical compound based on hydrated silicates or aluminosilicates of lamellar structure. Typically, the clay can be selected among amesite, antigorite, beidellite, berthierine, celadonite, chrysolite, cronstedtite, damouzeite, dickite, glauconite, halloysite, illite, kaolinite, lizardite, montmorillonite, muscovite, nacrite, nontronite, paragonite, pyrophyllite, sericite, vermiculite, and mixtures thereof, in particular among antigorite, chrysolite, damouzeite, halloysite, kaolinite, montmorillonite, nacrite, pyrophyllite, vermiculite, and mixtures thereof, more preferably kaolinite.

[48] Clay, in particular kaolinite, advantageously exhibits an anti-corrosion property. Corrosion of an element of the combustion unit, in particular the boiler, is caused by deposits of inorganic compounds present in certain wastes. Corrosion reduces the safety of the combustion unit and has a significant economic impact as it necessitates replacement of the corroded element of the combustion unit. Due to its anti-corrosion property, clay, in particular kaolin, makes it possible to maintain the safety of the combustion unit and reduces the replacement of elements of the combustion unit.

[49] For the purposes of the present invention, the term "bromine salt" is understood to mean a chemical compound comprising an anion and a bromide cation. Typically, the bromine salt can be selected among sodium bromide,

potassium bromide, calcium bromide, and mixtures thereof, in particular sodium bromide.

[50] Certain industrial wastes may contain mercury which is found in the combustion flue gas produced during incineration of these wastes. Due to the acute toxicity of mercury, the maximum value of mercury allowed in flue gas from combustion units is very low (0.05 mg/Nm^3). Under the operating conditions of the contact step a), bromine salt oxidizes the mercury present in the combustion flue gas to form oxidized mercury which can then easily be captured by activated carbon or acid scrubbers. Advantageously, bromine salt facilitates reduction of the mercury concentration in combustion flue gas.

[51] When the powder composition according to the invention further comprises an additive as defined above, it advantageously comprises, relative to the total weight of the composition, at least 50% of alkaline earth metal salt, in particular from 60% to 90% of alkaline earth metal salt, more particularly from 69% to 71% of alkaline earth metal salt, the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3, in particular from 0.15 to 0.25, more particularly from 0.20 to 0.22, and the mass ratio between the additive and the alkaline earth metal salt is from 0.05 to 0.3, in particular from 0.15 to 0.25, more particularly from 0.20 to 0.22.

[52] According to a variant of this particular embodiment, the additive is a clay and the powder composition comprises, relative to the total weight of the composition, at least 50% of alkaline earth metal salt, in particular from 60% to 90% of alkaline earth metal salt, more particularly from 69% to 71% of alkaline earth metal salt, the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3, in particular from 0.15 to 0.25, more particularly from 0.20 to 0.22, and the mass ratio between the clay and the alkaline earth metal salt is from 0.05 to 0.3, in particular from 0.15 to 0.25, more particularly from 0.20 to 0.22. Preferably the alkaline earth metal salt is calcium carbonate and the ammonium salt is ammonium sulfate.

[53] In this variant, the clay is preferably kaolinite. The powder composition may thus comprise kaolinite and, relative to the total weight of the composition, at least

50% of calcium carbonate, in particular from 60% to 90% of calcium carbonate, the mass ratio between the ammonium sulfate and the calcium carbonate is from 0.05 to 0.3, in particular from 0.15 to 0.25, and the mass ratio between the kaolinite and the calcium carbonate is from 0.05 to 0.3, in particular from 0.15 to 0.25.

- 5 **[54]** According to one particular variant, the powder composition can comprise kaolinite and, relative to the total weight of the composition, from 69% to 71% of calcium carbonate, the mass ratio between the ammonium sulfate and the calcium carbonate is from 0.20 to 0.22, and the mass ratio between the kaolinite and the calcium carbonate is from 0.20 to 0.22.
- 10 **[55]** At the end of step a) of placing the acid gases contained in the combustion flue gas in contact with the powder composition, the flue gas may comprise a residual concentration of acid gases. Thus, according to one particular embodiment, the method of the invention may comprise, after the contact step a), a step b) of neutralizing the residual acid gases in the flue gas resulting from step a).
- 15 **[56]** Step b) of neutralizing the residual acid gases is typically carried out at a temperature less than or equal to 250°C, by placing the flue gas from step a) in contact with lime, sodium bicarbonate, soda, a reducing agent such as ammonia or urea, and mixtures thereof.
- [57]** The contact between the flue gas from step a) and lime, sodium bicarbonate, 20 soda, and mixtures thereof, is particularly effective in reducing the residual concentration of HCl and/or SO₂.
- [58]** The contact between the flue gas resulting from step a) and an ammonia or urea type of reducing agent, and mixtures thereof, is particularly effective in reducing the residual concentration of NO_x. This contact may be followed by passage through 25 a selective catalytic reduction unit.
- [59]** The method according to the invention makes it possible to reduce the acid gas concentration in combustion flue gas, i.e. the flue gas produced by a combustion unit **1** as schematically represented in FIG. 1. A combustion unit **1** typically comprises, in the direction of flow, a combustion furnace **11**, for example rotary, a 30 flue gas post-combustion chamber **12**, a flue gas cooling unit comprising a boiler **13**

then a cooling tower **14**, a cooled flue gas neutralization unit **15**, a flue gas filtration unit **16**, a ventilation and flue gas extraction unit **17** and a chimney **18**.

[60] Typically, the waste incineration is carried out in the combustion furnace **11** during an incineration step. The incineration step is conventionally carried out at a temperature ranging from 850°C to 1000°C and produces the combustion flue gas which contains the acid gases. This flue gas is then sent to the post-combustion chamber **12** to be burned during a post-combustion step. The post-combustion step is conventionally carried out at a temperature close to the temperature of the incineration step. Typically, the temperature in the combustion furnace **11** is 850°C to 1200°C and the temperature in the post-combustion chamber **12** is 900°C to 1150°C.

[61] According to one particular embodiment, the contact step a) of the method according to the invention is carried out in the combustion furnace **11** and/or in the post-combustion chamber **12** of the combustion unit **1**.

[62] Indeed, the temperature during the incineration step in the combustion furnace **11** and/or during the post-combustion step in the post-combustion chamber **12** is such that the contact step a) of the method according to the invention can advantageously be carried out there.

[63] In this particular embodiment, it is therefore not necessary to add to the combustion unit **1** a unit specifically dedicated to reducing the acid gas concentration in the combustion flue gas. In addition, in this particular embodiment, it is not necessary to subsequently reheat the combustion flue gas in order to treat it. Thus, according to this particular embodiment, the energy efficiency of the method according to the invention is increased.

[64] Typically, the powder composition can be injected into the combustion furnace **11**, at the interface between the combustion furnace **11** and the post-combustion chamber **12**, and/or into the post-combustion chamber **12**.

[65] The powdery powder can be injected using an injection device such as a volumetric dosing screw, a weight-based dosing screw, or a microdose dosing screw.

[66] Because of its particle size distribution, the powder composition has flow properties that allow good injection.

[67] In one particular embodiment, step b) of neutralizing the residual acid gases in the flue gas resulting from contact step a) can be carried out in the cooled flue gas neutralization unit **15**.

[68] In this particular embodiment, it is therefore not necessary to add to the combustion unit **1** a unit specifically dedicated to neutralizing the residual acid gases in the flue gas resulting from contact step a). Thus, according to this particular embodiment, the energy efficiency of the method of the invention is increased.

[69] A second object of the invention is a powder composition comprising an alkaline earth metal salt and an ammonium salt.

[70] The powder composition according to the second object of the invention is as described above in relation to the method for treating combustion flue gas comprising acid gases, which is the first object of the invention.

[71] Unless otherwise indicated or in case of obvious incompatibility, the embodiments of the invention described above can be combined with each other.

[72] The invention is described in more detail below, with the aid of the following examples which are in no way limiting but are given solely as examples.

Examples

[73] This example describes an industrial test of the powder composition according to the invention carried out on a combustion unit **1** which is an existing hazardous waste incineration line.

[74] The combustion unit **1** used is represented in the diagram of FIG. 1 and is composed of the following elements:

- a rotary combustion furnace **11**,
- a post-combustion chamber **12**,
- a boiler **13** with injection of solid urea in the first leg,
- a flue gas cooling tower **14**,
- a cooled flue gas neutralization unit **15**,

- a flue gas filtration unit **16** comprising two bag filters,
- a ventilation and flue gas extraction unit **17**, and
- a chimney **18**.

[75] Lime is injected into the cooled flue gas neutralization unit **15**.

5 **[76]** For carrying out the tests, the tested powder composition comprises:

- 70% calcium carbonate,
- 15% ammonium sulfate, and
- 15% kaolin

and has a d90 value of 47.6 μm .

10 **[77]** The d90 value of the powder composition is determined according to the following protocol:

A sample of the powder composition is mixed with distilled water in an external ultrasonic tank and stabilized for 10 minutes.

The stabilized sample is introduced into a "small volume" measurement cell (120
15 ml) of a Malvern-Mastersizer 2000 laser particle size analyzer. The pump speed is 3000 rpm. The quantity of stabilized sample introduced and analyzed corresponds to obtaining a degree of laser obscuration in the red comprised between 15 and 17%.

The laser obscuration in the red is stabilized for 20 minutes before the measurement.

20 Despite this stabilization of 20 minutes, strong agglomeration is present but does not prevent the measurement from being carried out.

[78] The powder composition tested is stored in a 20-ton capacity silo. The injection at the bottom of the post-combustion chamber **12** (1st third) is done at two diametrically opposed points so as to optimize intimate contact between the powder
25 composition and the acid gases to be neutralized, namely SO₂, HCl, and NO_x. This injection is done through the use of a dosing screw located downstream of a load cell placed under the silo to control and regulate the mass flow rates of the injection. To do this, regulation with threshold values set at 150 mg/Nm³ for SO₂ and HCl (measurements taken at the outlet of the boiler **13**) is implemented with
30 corresponding mass flow rates varying from 20 kg/h to 200 kg/h depending on the

values measured above 150 mg/Nm³. In order to know the efficiency of the reduction of the concentrations of SO₂, HCl, and NO_x, measurements were carried out upstream, i.e. before injection of the powder composition tested, in the post-combustion chamber **12**, and downstream at the boiler outlet **13**.

5 **[79]** During the tests, the temperature in the combustion chamber is 950°C.

[80] [Table 1] shows all results obtained in thirteen tests with injection of the powder composition tested.

[81] [Table 1]

Test no.	[SO ₂] upstream (mg/Nm ³)	[SO ₂] downstr. (mg/Nm ³)	Efficiency (%)	[HCl] upstream (mg/Nm ³)	[HCl] downstr. (mg/Nm ³)	Efficiency (%)	[NO _x] upstream (mg/Nm ³)	[NO _x] downstr. (mg/Nm ³)	Efficiency (%)
1	937.5	247.2	73.6	961.2	523.1	45.6	923.6	61.7	93.3
2	837.6	229.3	72.6	720.2	460.9	36.0	476	82.2	82.7
3	1138	125.5	89.0	376.7	230.7	38.8	806	55	93.2
4	468.8	92.1	80.4	739.7	499.9	32.4	487.3	63.3	87.0
5	663.7	97.5	85.3	629.9	470.1	25.4	350.5	39.9	88.6
6	608.8	37.4	93.9	782	570.2	27.1	337.3	32.1	90.5
7	266.9	49.8	81.3	597.2	429.9	28.0	268.3	26.1	90.3
8	325.5	79.9	75.5	309.2	230.3	25.5	247.4	31	87.5
9	755.3	145.1	80.8	448	311.1	30.6	298.2	39.1	86.9
10	396.6	105.1	73.5	807.1	529.9	34.3	336.4	32.5	90.3
11	1259	168.3	86.6	1273	870.2	31.6	299.2	23.1	92.3
12	1350	375.2	72.2	1537	920.1	40.1	503.1	62.1	87.7
13	817.9	199	75.7	1649	998.2	39.5	334.1	40.9	87.8
			80.0			33.5			89.1

[82] It appears that:

- the average efficiency in reducing SO₂ concentrations is 80%,
- the average efficiency in reducing HCl concentrations is 33%, and
- the average efficiency in reducing NO_x concentrations is 89%.

5 **[83]** The powder composition tested therefore allows efficient reduction of HCl and highly efficient reduction of SO₂ and NO_x.

[84] In addition, the amount of lime injected into the cooled flue gas neutralization unit **15** during the thirteen tests is approximately four times less than the amount of lime that would have been injected into this neutralization unit **15** if
10 the powder composition tested had not been injected into the post-combustion chamber **12**.

[85] The powder composition tested therefore allows a significant reduction in the consumption of lime. It therefore allows a significant reduction in the costs and risks associated with this raw material and a reduction in costly maintenance
15 shutdowns.

Claims

[Claim 1] Method for treating combustion flue gas comprising acid gases, said method comprising a contact step a) of placing said acid gases in contact with a powder composition comprising an alkaline earth metal salt and an ammonium salt in an oxidizing atmosphere and at a temperature greater than or equal to 850°C, wherein the ammonium salt is selected among ammonium carbonate, ammonium chloride, ammonium sulfate, ammonium sulfide, and mixtures thereof, and wherein the powder composition comprises, relative to the total weight of the composition, at least 50% of alkaline earth metal salt, and the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3.

[Claim 2] Method according to claim 1, wherein the acid gases are selected among H_3PO_4 , CO_2 , NO_x , HCN , SO_2 , H_2S , HF , F_2 , HCl , Cl_2 , HBr , Br_2 , HI , I_2 , and mixtures thereof.

[Claim 3] Method according to claim 1 or claim 2, wherein the alkaline earth metal salt comprises a cation selected among a magnesium cation, a calcium cation, and mixtures thereof.

[Claim 4] Method according to one of the preceding claims, wherein the ammonium salt is ammonium sulfate.

[Claim 5] Method according to one of the preceding claims, wherein the powder composition comprises calcium carbonate and ammonium sulfate.

[Claim 6] Method according to claim 5, wherein the calcium carbonate comes from chalk, limestone, lime, industrial waste, and mixtures thereof.

[Claim 7] Method according to claim 6, wherein the industrial waste is mineral sludge.

[Claim 8] Method according to claim 7, wherein the mineral sludge is decarbonation sludge, sludge from primary brine purification, and a mixture thereof.

[Claim 9] Method according to one of the preceding claims, wherein the powder composition further comprises an additive, in particular an additive selected among a clay, a bromine salt, and mixtures thereof.

[Claim 10] Method according to claim 9, wherein the powder composition comprises a clay and, relative to the total weight of the composition, at least 50% of

alkaline earth metal salt, the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3, and the mass ratio between the clay and the alkaline earth metal salt is from 0.05 to 0.3.

[Claim 11] Method according to one of the preceding claims, wherein the contact step a) is carried out in a combustion furnace (11) and/or in a post-combustion chamber (12) of a combustion unit (1).

[Claim 12] Powder composition comprising an alkaline earth metal salt and an ammonium salt comprising, relative to the total weight of the composition, at least 50% of alkaline earth metal salt, and the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.05 to 0.3, and wherein the ammonium salt is selected among ammonium carbonate, ammonium chloride, ammonium sulfate, ammonium sulfide, and mixtures thereof.

[Claim 13] Powder composition according to claim 12, wherein the alkaline earth metal salt comprises a cation selected among a magnesium cation, a calcium cation, and mixtures thereof.

[Claim 14] Powder composition according to claim 12 or claim 13, wherein the ammonium salt is ammonium sulfate.

[Claim 15] Powder composition according to any one of claims 12 to 14, comprising calcium carbonate and ammonium sulfate.

[Claim 16] Powder composition according to claim 15, wherein the calcium carbonate comes from chalk, limestone, lime, industrial waste, and mixtures thereof.

[Claim 17] Powder composition according to claim 16, wherein the industrial waste is mineral sludge.

[Claim 18] Powder composition according to claim 17, wherein the mineral sludge is decarbonation sludge, sludge from primary brine purification, and a mixture thereof.

[Claim 19] Powder composition according to any one of claims 12 to 19, further comprising an additive, in particular an additive selected among a clay, a bromine salt, and mixtures thereof.

[Claim 20] Powder composition according to claim 19, comprising a clay and, relative to the total weight of the composition, at least 50% of alkaline earth metal

salt, the mass ratio between the ammonium salt and the alkaline earth metal salt is from 0.1 to 0.3, and the mass ratio between the clay and the alkaline earth metal salt is from 0.1 to 0.3.