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(54) Title : SOLID INORGANIC COMPOSITION, METHOD FOR PREPARING SAME, AND USE THEREOF FOR REDUCING DIOXINS AND HEAVY METALS IN FLUE GASES

(54) Titre : COMPOSITION SOLIDE MINÉRALE, SON PROCEDE DE PRÉPARATION ET SON UTILISATION EN ABATTEMENT DE DIOXINES ET METAUX LOURDS DES GAZ DE FUMÉES

(57) Abstract : The invention relates to a solid inorganic composition for reducing dioxins and furans, as well as heavy metals, in particular mercury, present in flue gases, to a method for preparing such a composition, and to the use thereof for reducing dioxins and furans as well as heavy metals, in particular mercury, present in flue gases, by contacting said flue gases with said solid inorganic composition.

(57) Abrégé : Composition solide minérale d'abattement de dioxines et furanes ainsi que de métaux lourds, notamment de mercure, présents dans les gaz de fumées, le procédé de préparation d'une telle composition et son utilisation pour l'abattement de dioxines et furanes ainsi que de métaux lourds, notamment de mercure, présents dans les gaz de fumées, par mise en contact des gaz de fumées avec ladite composition solide minérale.

SOLID INORGANIC COMPOSITION, METHOD FOR PREPARING SAME AND
USE THEREOF FOR REDUCING DIOXINS AND HEAVY METALS IN FLUE
GASES

5 The present invention relates to a composition for reducing heavy metals and dioxins in flue gases comprising a solid absorption material which is a minimal compound, preferably non-functionalized, selected from ~~phylosilicates~~ of the "palygorskite-sepiolite" group, according to the Dana classification.

10 Dioxins and furans as well as heavy metals, notably mercury, are toxic compounds present in flue gases, notably in the gas state and the emission of which is generally strictly regulated. In the sense of the invention, the term of "dioxin" will be used in the generic sense, including dioxins as well as furans and possibly other analog compounds, notably precursors of dioxins and furans such as polycyclic aromatic hydrocarbons (PAH). Indeed, standards in this regard generally group the whole of the 15 dioxins (75 species) and of the furans (135 species) into a single "toxic equivalent" concentration (TEQ), expressed relatively to the most toxic dioxin molecule.

20 By the terms of "heavy metals", are mainly meant metals having a density of more than 5,000 kg/m³, notably the most common heavy metals, generally being subject to regulations, i.e. lead, chromium, copper, manganese, antimony, arsenic, cobalt, nickel, vanadium cadmium, thallium and mercury, preferably lead, thallium, cadmium and mercury in particular mercury. These metals may appear in the elementary state or in ionic form.

25 The reduction of dioxins and heavy metals present in flue gases is generally performed in the state of the art by means of carbonaceous compounds, such as active coals, lignite cokes or the like. The selection of the type(s) of carbonaceous compounds depends on the predominance of dioxins on the one hand or of heavy metals on the other hand, in pollutants to be reduced and on respective regulations to be met for both of these types of pollutants.

30 For example, document WO 2006/099291 discloses the reduction of mercury of flue gases by using a catalytic adsorbent in the form of a carbonaceous compound doped with halogenated compounds. More particularly, a halide salt is dispersed on active coal and the catalytic oxidation activity of the active coal promotes the formation of a mercury halide. An oxidant oxidizes the mercury and the anion of the doping compound provides a counter-ion for the mercury ion oxidized by the oxidant. As 35 this is observed, the presence of an oxidant is therefore essential in this type of

exclusively relate to liquids such as water or to gases such as oxygen or possibly butane or the like.

Document DE 198 24 237 as for it discloses mineral compounds to which are additives added for capturing mercury. The disclosed additives are generally sulfur-containing compounds, providing with this, a teaching similar to the aforementioned Spanish references. Mention is also made of the use of chlorides which are mineral phyllosilicates from the group of chlorides.

As this is seen, the prior art provides substitutes for carbonaceous compounds for purifying flue gases but the proposed solutions either relate to the reduction of dioxins or to the reduction of heavy metals.

Patent EP 1732668 B1 provides the use of non-functionalized mineral compounds of the "palygorskite-sepiolite" group according to the Dana classification for reduction of heavy metals, in particular mercury. However, the efficiency of sepiolite for reducing mercury seems to be limited, as compared with active coals, a priori requiring overdosage.

The object of the invention is to find a remedy to the drawbacks of the prior art, by providing a composition as mentioned at the beginning in which said mineral compound is doped with a halide salt. <1>

Indeed, it was observed very unexpectedly and in an unpredictable way that this mineral compound doped with a halide as a salt allowed joint and effective reduction of dioxins and of heavy metals, notably in the gas state, present in flue gases, by using a same and single mineral compound, the manufacturing and the application of which are simple and not dangerous.

The effect of this composition according to the invention on the reduction rate of dioxins and of heavy metals is particularly unexpected for the following reasons. Measurements of the BET specific surface area and of the BJH pore volume, directly carried out on the doped mineral compound, show a sometimes significant decrease of these two characteristics, at the very least with a strong dopant salt content. Moreover, it is conceivable that crystallization of a salt on a porous support should modify the accessibility to the pores for molecules of large size such as dioxins. Finally, by covering the surface of a porous solid even partially, with a compound of a different nature, it is possible to modify the adsorption capacity for molecules such as dioxins. These elements suggest a risk of reduction of the performances for reducing the doped mineral compound relatively to the non-doped mineral compound, since it is known that the capacities for reducing dioxins and heavy metals are directly influenced by the

4 bls

- 5 <1> = said mineral compound is selected from phyllosilicates of the "palygorskite-sepiolite" group according to the Dana classification, said mineral compound being doped with a halide salt and retaining the initial crystalline structure, said halide salt being present in an amount on a dry basis ranging from 0,5% to 20% by weight on the basis of the weight of the composition.

aforementioned elements.

In a particular embodiment, the mineral compound is selected from the group of phyllosilicates of the sub-group of sepiolite according to the Dana classification.

The phyllosilicates targeted by the invention have high porosity, typically a pore volume comprised between 0.20 and 0.60 cm³/g, notably between 0.25 and 0.40 cm³/g, measured by the BJH method, applied to the nitrogen desorption isotherm, obtained at the temperature of liquid nitrogen (77 K). This pore volume interval is valid for pores with a size comprised between 2 and 100 nanometres. Moreover, these phyllosilicates typically have a specific surface area from 100 to 200 m²/g, particularly from 110 to 160 m²/g.

By "mineral compound doped with a halide salt" is meant an aforementioned mineral compound, for which the surface accessible to flue gases is partly or completely covered with halide salt.

The surface accessible to the gas not only comprises the external surface of the particles making up the mineral compound but also a portion or the whole of the internal surface of these partially porous particles.

The mineral compound doped with a halide salt contains on a dry basis, from 0.5% to 20%, preferably, from 1% to 15%, in particular, from 1.5% to 10% by weight of halide salt based on the weight of the composition according to the invention. The halide salt may be an alkaline or earth alkaline halide, notably NaCl, NaBr or NaI, KCl, KBr or KI, CaCl₂, CaBr₂ or CaI₂, MgCl₂, MgBr₂ or MgI₂, or further NH₄Cl, NH₄Br or NH₄I or one of their mixtures.

In a particular embodiment according to the invention, the mineral compound doped by said halide salt has a BET specific surface area comprised between 70 and 170 m²/g, often between 80 and 140 m²/g and in particular between 90 and 130 m²/g.

Preferably, the mineral compound doped by said halide salt has a pore volume comprised between 0.15 and 0.32 cm³/g, preferably between 0.20 and 0.30 cm³/g and more preferentially between 0.22 and 0.28 cm³/g, as measured by the BJH method, applied to the nitrogen desorption isotherm, obtained at a temperature of liquid nitrogen of about 77K for pores with a size comprised between 2 and 100 nm.

Advantageously, the mineral compound according to the invention is in powdery form, i.e. the size of the particles is in majority (more than 90%) smaller than 1 mm and essentially greater than 1 µm, i.e. it preferably has a d₉₀ of less than 1 mm.

By d₉₀ is meant the interpolated value of the distribution curve of the

latter is deagglomerated and dried in a cage mill/dryer, by means of hot gases at about 400-450°C and a dwelling time such that the gases leave the mill/dryer at about 150°C. A dried sepiolite according to the invention is obtained with 5% by weight of KBr, based on the weight of the composition.

5 The thereby doped sepiolite is used in a line for treating 7t/h of waste from an incinerator of domestic waste, producing about 43,000 Nm³/h of fumes to be treated. The doped sepiolite is metered by means of a screw and injected pneumatically into the gas current at 150°C in an amount of 3kg/h, and then collected in a sleeve filter, notably with the combustion dust.

10 The mercury concentrations are measured upstream from the point of injection of the doped sepiolite and downstream from the sleeve filter by atomic absorption (MERCEM from Sick-Maihak). The measured concentrations, normalized on dry gases and referred to 11% of oxygen are:

15 - 85 µg/Nm³ upstream and
- 14 µg/Nm³ downstream from the sleeve filter. This result is clearly less than the 50 µg/Nm³ of the regulations in effect and shows a mercury reduction rate of 84%.

20 At the same time as the measurement of the mercury content, the dioxin content was measured at the chimney, by an approved organization according to the EN 1948 (1997) and ISO 9096 (2003) standards. The obtained value is 0.04ng TEQ/Nm³ on dry gases and reduced to a concentration of 11% of O₂. This result perfectly observes the regulations for emissions of 0.1ng TEQ/Nm³ under dry conditions, reduced to 11% of O₂.

Example 9-8 - industrial scale

25 The same doped sepiolite as in Example 10 is used in a line for treating 7 t/h of waste from a domestic waste incinerator, producing about 43,000 Nm³/h of fumes to be treated. The doped sepiolite is metered by means of a screw and injected pneumatically into the gas stream at 180°C in an amount of 8 kg/h, and then collected in a sleeve filter, notably with the combustion dusts.

30 The mercury concentrations were measured downstream from the sleeve filter by atomic absorption (MERCEM from Sick-Maihak). The measured mercury concentrations normalized on dry gases and referred to 11% of oxygen are from 0.1 µg/Nm³ to 0.8 µg/Nm³. These results are clearly less than the 50 µg /Nm³ of the regulations in effect.

35 The dioxin content was measured at the chimney, by an approved

CLAIMS

1. A composition for reducing heavy metals and dioxins in flue gases comprising a solid sorption material which is a mineral compound, preferably non-functionalized, characterized in that said mineral compound is selected from phyllosilicates of the "palygorskite-sepiolite" group according to the Dana classification, characterizing that said mineral compound is being doped with a halide salt and retaining the initial crystalline structure, said halide salt being present in an amount on a dry basis ranging from 0.5% to 20% by weight on the bases of the weight of the composition.

10 2. The composition according to claim 1, wherein said mineral compound is selected from the group of phyllosilicates from the subgroup of sepiolite according to the Dana classification.

15 3. The composition according to claim 1 or claim 2, wherein said halide salt is an alkaline halide, an earth alkaline halide or the like, preferably selected from the group consisting of NaCl, NaBr, NaI, KCl, KBr, KI, CaCl₂, CaBr₂, CaI₂, MgCl₂, MgBr₂, MgI₂, NH₄Cl, NH₄Br or NH₄I or mixtures thereof.

20 4. The composition according to any of the preceding claims, wherein said halide salt is present in an amount on a dry basis ranging from 0.5% to 20% by weight, preferably from 1% to 15% by weight and in particular from 1.5% to 10% by weight of halide salt on the basis of the weight of the composition.

5. The composition according to any of the preceding claims, wherein the mineral compound doped by said halide salt has a BET specific surface area comprised between 70 and 170 m²/g, preferably between 80 and 140 m²/g and more preferentially between 90 and 130 m²/g.

25 6. The composition according to any of the preceding claims, wherein said mineral compound doped by said halide salt has a pore volume comprised between 0.15 and 0.32 cm³/g, preferably between 0.20 and 0.30 cm³/g and more preferentially between 0.22 and 0.28 cm³/g, as measured by the BJH method, applied to the nitrogen desorption isotherm.

30 7. A method for manufacturing a composition for reducing heavy metals and dioxins comprising the steps:

- supplying a solid sorption material which is a mineral compound, preferably non-functionalized, selected from phyllosilicates from the "palygorskite-sepiolite" group according to the Dana classification,

- supplying a halide salt, and
- putting into contact said mineral compound and said halide salt with formation of a mineral compound doped with the halide salt.

8. The method according to claim 7, wherein said contacting of said
5 mineral compound and of said halide salt is achieved with stirring.

9. The method according to claim 7 or claim 8 wherein said supplied
mineral compound has a humidity comprised between 0.1 and 100 g/kg, advantageously
between 2 and 90 g/kg.

10. The method according to any of claims 7 to 9, wherein said contacting
10 is carried out at room temperature.

11. The method according to any of claims 7 to 10, wherein said halide
salt is in liquid form, in an aqueous phase.

12. The method according to any of claims 7 to 11, wherein said step for
putting into contact said mineral compound and said halide salt is spraying of said halide
15 salt on said mineral compound optionally with stirring.

13. The method according to claim 11, wherein said step for putting into
contact said mineral compound and said halide salt is soaking of said mineral compound
in said halide salt in a liquid phase, optionally with stirring.

14. The method according any of claims 11 to 13 wherein said halide salt
20 in a liquid phase is an aqueous solution or not, having a halide salt content comprised
between 1% and 30%, in particular between 5% and 27%, preferably between 10% and
27% by weight based on the total weight of said solution.

15. The method according to one of claims 7 to 14, further comprising one
or more steps for drying and/or deagglomerating said mineral compound doped with the
25 halide salt, preferably at a temperature comprised between 60 and 200°C, in particular
between 75 and 170°C.

16. The method according to any of claims 7 to 15, wherein said halide salt
is an alkaline halide, an earth alkaline halide or the like, preferably selected from the
group consisting of NaCl, NaBr, NaI, KCl, KBr, KI, CaCl₂, CaBr₂, CaI₂, MgCl₂, MgBr₂,
30 MgI₂, NH₄Cl, NH₄Br or NH₄I or mixtures thereof.

17. The use of the composition according to any of claims 1 to 6, for
reducing dioxins and heavy metals, preferably in the gas state, in particular mercury and
most particularly mercury Hg⁰ in flue gases.

18. The use according to claim 17, as a mixture with a basic reagent such
35 as lime.