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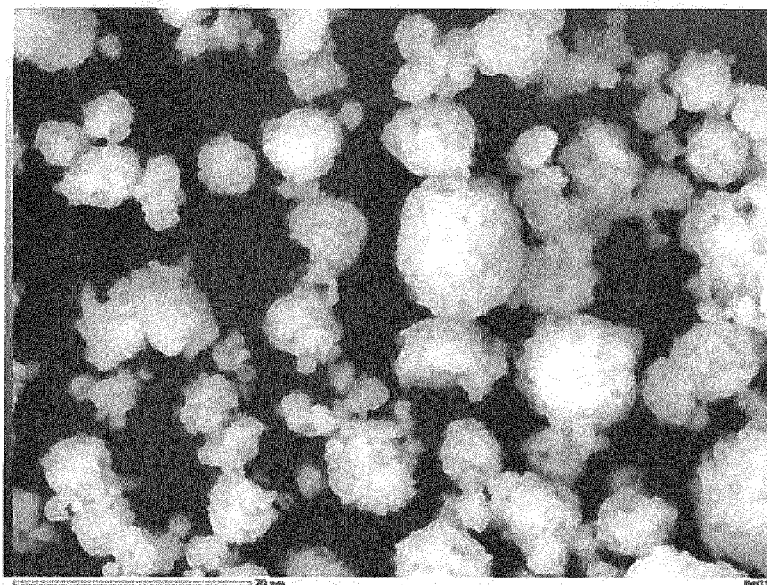
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(54) Title: LIME-BASED SORBENT COMPOSITION FOR MERCURY REMOVAL AND ITS MANUFACTURING PROCESS

**Fig. 1**

(57) Abstract: Sorbent composition containing core-shell particles for removing heavy metals, in particular, mercury from gases, wherein the core comprises a calcium-magnesium compound fitting the formula

$a\text{CaCO}_3 \cdot b\text{MgCO}_3 \cdot x\text{CaO} \cdot y\text{MgO} \cdot z\text{Ca}(\text{OH})_2 \cdot t\text{Mg}(\text{OH})_2 \cdot u\text{I}$, wherein I represents impurities, a, b, x, y, z and t each being mass fractions ≥ 0 and $\leq 100\%$, u being mass fraction ≥ 0 and $\leq 20\%$ by weight, and is coated with a shell presenting a thickness comprised in the range of 50 nm to 20 μm , and comprising at least a metal salt and a sulfur-based compound and its manufacturing process.

**« LIME-BASED SORBENT COMPOSITION FOR MERCURY REMOVAL AND ITS
MANUFACTURING PROCESS »**

The present invention relates to a sorbent composition containing particles for removing heavy metals, in particular mercury, from flue gases.

Sorbent composition containing solid particles are well known
5 in the art.

Document US7923397B2 discloses a modified activated carbon sorbent (with a powder of elementary sulfur) to remove heavy metals from flue gases. While activated carbon is the best available sorbent technique up to now in terms of mercury uptake (quantity of mercury adsorbed per gram of
10 sorbent), carbon is susceptible to combustion inside the flue gas stream, which is one of the main drawbacks of this sorbent.

Further, the use of activated carbon sorbent increases the total organic carbon content in the dusts present at the discharge of these flue gases, which carbon content is nowadays strictly regulated.

15 Additionally, the carbon colors the gypsum produced from wet desulfurization process black while the whiteness of this material determines its valorization value when selling it to gypsum manufacturer.

Further, activated carbon is naturally retained in the fly ash waste stream. However, activated carbon can adversely interact with the
20 additives used in cement and concrete formulations precluding by consequence the utilization of said fly ash containing activated carbon as additive in the cement industry that must therefore rather be disposed of, at significant cost.

For those reasons, there is a need to provide alternatives to the
25 use of activated carbon, which should be more competitive in terms of costs, for acquiring it, but also for handling by-products and valorizing the residual material of the flue gases treatment.

Document US2014/0050641A1 relates to an aqueous mercury sorbent composition. Such composition is produced by mixing

(a) an aqueous solution of a silica containing precursor (such as silicic acid, colloidal silica);

5 (b) an aqueous solution of metal species (such as copper salts);
and

(c) a solution of a sulfur-based species (such as (poly)sulfide salts or dithiocarbamates) with

(d) process water.

10 Unfortunately, such impregnated silica involves quite complex manufacturing process and is sold on the market as being a quite expensive specialty product, especially, where the silica has to be highly porous for good capture properties, while on the other hand it is intended to treat waste product. Therefore, even if this solution is quite well accepted on the market,
15 notably because up to now no other mineral sorbent composition efficient enough has been proposed, it remains a problem for industrial actors to use expensive silica to treat flue gases being a waste.

In addition, according to this document, the sorbent composition is intended to be used under aqueous suspension in two
20 different applications. In the first application, the aqueous suspension is designed to be used in wet flue gas desulfurizer units, where it is stable enough. In the second application, the aqueous suspension is injected in the dry and hot flue gas. However, in the latter case, the aqueous suspension is dried in the hot flue gas causing likely in such a case a loss of efficiency due to
25 sensitivity towards thermal decomposition and a lack of reproducibility since the drying process of the sorbent is only undergone and not controlled. Indeed, tests conducted in our study have proven that spray-dried colloidal silica particles have a tendency to trap active chemical compounds into the particle core during the spray-drying step, thus reducing overall efficiency.

30 Also, the lack of reproducibility from one plant to another, as well as the difficulties linked with the handling and injection of liquid additive

in a process dealing with hot gas, are other issues encountered with this type of product.

Document WO2014/164975A1 discloses also a sorbent for removing mercury or sulfur from gas stream. Such composition is disclosed as
5 being a solid state composition of

(a) an inorganic base (such as calcium hydroxide, sodium sesquicarbonate, sodium (bi)carbonate, potassium carbonate and/or calcium carbonate); and

(b) a sulfide (such as ammonium sulfide, alkali metal sulfide,
10 alkali-earth metal sulfide and/or transition metal sulfide); and

(c) optionally a support (such as silicate, aluminate, aluminosilicate, and/or carbon) carrying the admixture.

Unfortunately, all the sorbent compositions for mercury removal available on the market present drawbacks since either they consist
15 of organic sorbent material and have accordingly a high efficiency in terms of mercury removal but present ignition risks, or they are globally mineral but have a poor efficiency in terms of mercury removal and/or typically are expensive and/or may suffer from thermal decomposition in the range of high temperatures.

20 There is still therefore a need to provide a mineral sorbent composition, powerful for mercury removal from flues gases, thermally and chemically stable, affordable on a cost basis and compatible with fly ash valorization.

The present invention relates more precisely to sorbent
25 composition containing particles for removing heavy metals, in particular mercury, from flue gases, wherein said particles are core-shell particles with the aim to solve at least a part of the aforementioned drawbacks by providing a composition for an oxidative sorbent material used in the capture of heavy metals, and more specifically mercury, in both ionic and metallic form, and its
30 method of manufacturing. The heavy metals can be removed from a fluid, preferentially a gaseous fluid, notably from flue gas, wherein the heavy metals

are usually gaseous, in coal-fired plants, municipal solid waste incinerators, and/or cement kilns and/or other industries exhaust gases.

To solve this problem, it is provided according to the present invention, a lime-based sorbent composition wherein the core comprises a
5 calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{I}$, wherein I represents impurities, a, b, x, y, z and t each being mass fractions ≥ 0 and $\leq 100\%$, u being mass fraction ≥ 0 and $\leq 20\%$ by weight, based on the total weight of said at least one calcium-magnesium compound, characterized in that said core is
10 coated with a shell presenting a thickness of less than $20\text{ }\mu\text{m}$ and greater than 50 nm , shielding the core from the flue gases medium and comprising at least a metal salt and a sulfur-based compound.

According to the present invention, the CaCO_3 , MgCO_3 , CaO , MgO , $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ contents in calcium-magnesium compounds may
15 easily be determined with conventional methods. For example, they may be determined by X fluorescence analysis, the procedure of which is described in the EN 15309 standard, coupled with a measurement of the loss on ignition and a measurement of the CO_2 volume according to the EN 459-2:2010 E standard.

20 The impurities I notably comprise all those which are encountered in natural limestones and dolomites, such as clays of the silico-aluminate type, silica, impurities based on iron or manganese,... or those coming from the manufacturing process of the calcium-magnesium compound.

25 Tests conducted in our study have proven, when experimenting mixture of hydrated lime with sulfur-based compound, that lime, when in contact with the flue gases, either present on the surface or in mixture with the sulfur-based compound, has a strong tendency to reduce ionic mercury into elemental mercury, thereby yielding to a loss of efficiency in mercury
30 removal since mercury must be in the ionic form to react with the sulfur compound. In the present document, hydrated lime means an industrial

calcium-magnesium compound made essentially of calcium dihydroxide $\text{Ca}(\text{OH})_2$ with impurities.

Surprisingly, according to the present invention, due to the core-shell structure of the calcium-magnesium particles coated with a shell presenting a thickness of more than 50 nm and less than 20 μm , the negative effect of lime is reduced, thereby increasing drastically the mercury removal capacity of the composition according to the present invention.

Indeed, in the product of the present invention, the core of calcium-magnesium particles is totally shielded from the mercury compounds by the shell layer of sulfurous compound.

Moreover, the presence of an alkaline lime core (calcium-magnesium compound) helps to improve the stability of the sulfurous compound in the shell layer in its most reactive form being S^{2-} while at the same time preventing H_2S emissions resulting from acidic conditions.

Therefore the sulfur-based compound in the shell can react with ionic mercury present in the flue gases and form HgS .

In a preferred embodiment, in the lime-based sorbent composition according to the present invention, said sulfur-based compound is fitting the formula $\text{A}_\alpha\text{S}_\beta\text{O}_\gamma$ wherein α , β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture. In particular, said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture.

Therefore, the lime-based composition according to the present invention is mainly from inorganic nature, thereby helping to reduce the global carbon content in the fly ash.

In a particular embodiment of the present invention, in the lime-based sorbent composition according to the invention, said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

In a preferred embodiment, said metal salt is a copper halide, preferably a copper chloride.

In an alternative embodiment according to the present invention the lime-based sorbent composition according to the invention
5 further comprises a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.

Further, in another preferred embodiment according to the present invention, the lime-based sorbent composition according to the
10 invention further comprises a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docetyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and their mixtures.

In an advantageous lime-based sorbent composition according
15 to the invention, in the calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{l}$, $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

20 In another advantageous lime-based sorbent composition according to the invention, in the calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{l}$, $z \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one
25 calcium-magnesium compound.

Therefore, most of the core particles in the lime-based sorbent composition are made from hydrated lime, also called slaked lime, meaning that some particles might have a core being entirely slaked lime particles or a mixture of slaked and quicklime in the same core or even partially slaked lime
30 particles; to a level such that the amount of slaked lime with respect to the calcium-magnesium particles is greater than 60 w%.

Said at least one calcium-magnesium compound according to the present invention is therefore at least formed with slaked lime, slaked dolomitic lime, magnesium slaked lime or burnt dolime from the calcination of natural limestones or dolomites.

5 The composition according to the invention may therefore also comprise calcium or magnesium carbonates such as unburnt materials from the calcination of natural limestones or dolomites or else further products from the recarbonation of calcium-magnesium compounds. Finally it may also comprise calcium or magnesium oxides from the partial hydration (slaking) of
10 calcium-magnesium compounds.

In another variant according to the present invention, the calcium-magnesium compound of the lime-based sorbent composition presents a particle size distribution wherein d_{10} is comprised in the range from 0,5 to 3 μm , preferably from 0,75 to 2 μm ; d_{90} is comprised in the range from
15 7 to 50 μm , preferably from 10 to 40 μm , d_{50} is comprised in the range from 3 to 50 μm , preferably from 4 to 30 μm .

The notation d_x represents a diameter expressed in μm , relatively to which X % by mass of the measured particles are smaller or equal.

In yet another advantageous embodiment of the lime-based
20 sorbent composition according to the present invention, said shell presents a thickness of less than 10 μm , preferably less than 5 μm , in particular less than 2 μm , and greater than 100 nm, preferably greater than 200 nm, in particular greater than 300 nm.

It is well understood that the smaller the core particle, the
25 higher is its external surface, enabling therefore a higher amount of sulfur additive to be available in the outer layer, for a given sulfur/calcium-magnesium compound (core) ratio. This should improve the global mercury uptake.

However, tests have shown, in particular with hydrated lime
30 core, that too small core particles are undesirable since they tend to agglomerate together, trapping therefore some of the sulfur additive inside

the agglomerates, which will consequently decrease the global mercury uptake.

In a particularly advantageous embodiment according to the present invention, the ratio between calcium-magnesium compound (core) and sulfur ranges from 15:1 w/w to 1:1 w/w and preferably is of 2,5:1 w/w in the lime-based sorbent composition.

In another advantageous embodiment, the ratio between calcium-magnesium compound (core) and said metal salt ranges from 15:1 w/w to 1:1 w/w and preferably is of 5:1 w/w in the lime-based sorbent composition according to the invention.

Other embodiments of the lime-based sorbent composition according to the present invention are mentioned in the appended claims.

The present invention also relates to a process to produce a lime-based sorbent composition comprising the steps of :

i) Mixing a metal ammonia complex with an aqueous suspension of calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{I}$, wherein I represents impurities, a, b, x, y, z and t each being mass fractions ≥ 0 and $\leq 100\%$, u being mass fraction ≥ 0 and $\leq 20\%$ by weight, based on the total weight of said at least one calcium-magnesium compound, for a predetermined first period of time sufficient to ensure complete dispersion of metal on the calcium-magnesium particles, to form a suspension of calcium-magnesium particles onto which said metal is dispersed,

ii) Mixing said suspension of calcium-magnesium particles onto which said metal is dispersed with a calcium-magnesium polysulfide solution for a second predetermined period of time to form a lime-based composition pre-mix,

iii) Feeding said lime-based composition pre-mix into a spray-dryer to form a spray dried lime-based composition presenting particles being core-shell particles, wherein the core comprises said calcium-magnesium compound, said core being further coated with a shell presenting a thickness of more than 50 nm and less than 20 μm , shielding the

core from the flue gases medium and comprising at least a metal salt and a sulfur-based compound.

Preferably, said metal ammonia complex is obtained by mixing a metal salt with an ammonia solution, where the ratio between said metal salt and said ammonia ranges from 1:2 w/w to 1:10 w/w and preferably is of 1:5,5 w/w.

Advantageously, said calcium-magnesium polysulfide solution is obtained by mixing a sulfur-based compound with a calcium-magnesium compound fitting the formula $p\text{CaO} \cdot q\text{MgO} \cdot r\text{Ca}(\text{OH})_2 \cdot s\text{Mg}(\text{OH})_2 \cdot u\text{I}$, wherein I represents impurities, u being mass fractions ≥ 0 and $\leq 20\%$, p, q, r and s each being mass fractions ≥ 0 and $\leq 100\%$, with $p + q + r + s \geq 60\%$ by weight, based on the total weight of said at least one calcium magnesium compound to form said calcium-magnesium polysulfide solution.

Particularly, in the process according to the present invention, said aqueous suspension of calcium-magnesium compound, also called milk of calcium-magnesium compound, presents a solid content between 30 and 45 w% with respect to the total weight of the suspension of calcium-magnesium compound.

Advantageously, in the process according to the present invention, the aqueous suspension of calcium-magnesium compound comprises particles having a particle size distribution wherein d_{50} is comprised in the range from 0,5 to 20 μm , preferably from 0,5 to 10 μm and more preferably from 1 to 2,5 μm .

In a particular embodiment according to the present invention, said sulfur-based compound is fitting the formula $A_\alpha S_\beta O_\gamma$ wherein α , β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture. In particular, said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture..

Advantageously, said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

In a preferred embodiment, said metal salt is a copper halide,
5 preferably a copper chloride.

In a variant of the process according to the present invention, the process further comprises a step of adding a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium
10 halides and their mixtures.

Such doping agent can be added either to the spray dried lime-based composition, meaning after the spray drying, or to the calcium-magnesium polysulfide solution, preferably to the calcium-magnesium polysulfide solution.

In another variant of the process according to the present invention, the process further comprises a step of adding a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docetyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and
20 their mixtures.

Such dispersing agent is preferably added to the aqueous suspension of calcium-magnesium compound either before, after or simultaneously with the metal ammonia complex.

Preferably, in the calcium-magnesium compound fitting the
25 formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{l}$, $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

In another advantageous embodiment of the invention, in the
30 calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{l}$, $z \geq 60\%$, preferentially $\geq$

70%, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

More particularly, in the process according to the present invention, said shell presents a thickness of less than $10\text{ }\mu\text{m}$, preferably less than $5\text{ }\mu\text{m}$, in particular less than $2\text{ }\mu\text{m}$, and greater than 100 nm , preferably greater than 200 nm , in particular greater than 300 nm .

In a preferred embodiment of the process according to the present invention, the ratio between calcium-magnesium compound and sulfur ranges from 1:1 w/w to 1:2 w/w, preferably of 1:1,5 w/w in the calcium-magnesium polysulfide composition.

In another preferred embodiment according to the present invention, the ratio between said calcium-magnesium compound and said metal salt ranges from 15:1 w/w to 1:1, preferably is 5:1 w/w in the suspension of calcium-magnesium particles onto which the metal is dispersed.

Preferably, the calcium-magnesium compound presents a specific surface area measured by manometry with adsorption of nitrogen after degassing *in vacuo* at 190°C for at least 2 hours and calculated according to the multipoint BET method as described in the ISO 9277:2010E standard comprised between $5\text{ m}^2/\text{g}$ and $50\text{ m}^2/\text{g}$.

Other embodiments of the process according to the present invention are mentioned in the appended claims.

Other characteristics and advantages of the present invention will be derived from the non-limitative following description, and by making reference to the examples and the drawings.

Figure 1 represents a SEM picture of the particles of the sample "product 1" (obtained from example 1), showing core-shell particles of $\text{CuCl}_2/\text{CaS}_x$ supported on lime. The particles exhibit a mean diameter around $5\text{ }\mu\text{m}$, the particle size measuring typically between 1 and $10\text{ }\mu\text{m}$.

Figure 2 is a schematic presentation of the device used to measure the mercury capture with the several samples according to the invention and the one of the comparative examples.

Figure 3 represents the results of example 1.

Figure 4 represents the results of example 2.

Figure 5 represents the results of comparative example 1.

Figure 6 represents the results of comparative example 2.

Figure 7 represents the results of comparative example 3.

5 In the drawings, the same reference numbers have been allocated to the same or analog elements.

The invention concerns a sorbent under the form of a lime-based composition for the cleaning of waste gases charged with gaseous heavy metal, especially mercury, comprising :

10 a) a calcium-magnesium compound being a support (for instance calcium-magnesium compound at least formed with slaked lime, slaked dolomitic lime, magnesium slaked lime, but which may also comprise calcium or magnesium carbonates or oxides),

b) a metal salt (such as salts of titanium, vanadium,
15 manganese, iron, nickel, copper, zinc, and their mixture and preferably copper chloride), and

c) a sulfur-containing compound (such as sulfide salts, dithiocarbamates, sulfate salts, polymer-based dithiocarbamate, polysulfide salts and their mixture; preferably calcium sulfide, calcium polysulfide,
20 calcium sulfate and their mixture and more preferably calcium polysulfide).

Advantageously, a doping agent (such as alkali metal halides, alkali earth metal halides, ammonium halides and their mixtures, preferably sodium, potassium, calcium or magnesium halides) can be added either to the spray dried lime-based composition or to the calcium-magnesium polysulfide
25 solution, preferably to the calcium-magnesium polysulfide solution.

Optionally, a dispersant can be mixed with the suspension of calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{l}$ (such as (poly)sulfates, (poly)sulfonates, (poly)phosphates, (poly)phosphonates, polyols, and their
30 mixtures, preferably diethylenetriamine-penta(methylene phosphonic acid) (DTPMP) or sodium docetyl sulfate).

The sorbent is a powder in particular synthesized through spray drying and is notably composed of spherical particles exhibiting a core-shell structure wherein the calcium-magnesium compound making the support is the core and wherein the metal salt and sulfur-compound compose the shell.

5 The particle size distribution of this sorbent shown in Figure 1 is preferably as follows: $d_{10}=1\mu\text{m}$ and $d_{90}=10\mu\text{m}$, with d_{50} equal to $5\mu\text{m}$.

The preferred embodiment of the process according to the present invention is as follows:

i) a calcium polysulfide solution is prepared separately. This
10 chemical compound has been well known for a number of years. Its production requires a basic mix of lime and elemental sulfur, both being dissolved in boiling water (80°C - 100°C), stirred at 300 rpm for 2 hours. The ratios between lime and sulfur can vary (from 1:1 w/w to 1:2). Additional chemicals can be used as well (polyphosphonate for example). For this step
15 process, any hydrated lime or quicklime can be used (standard hydrated lime or with high surface area and/or high pore volume).

ii) Copper chloride is dissolved in water with ammonia (1:3 to
1:6 w/w) to form copper ammonia complex, stable at high pH. This solution is then mixed with a milk of lime (aqueous suspension of hydrated lime in
20 water) for several hours to ensure complete dispersion of copper on the lime particles. For this step process, it is advantageous to use fine milk of lime (meaning with a particle size distribution with a d_{10} between 0,5 and $1,5\mu\text{m}$; a d_{50} between 2 and $4\mu\text{m}$ and a d_{90} between 5 and $10\mu\text{m}$) and highly concentrated with solid content of 45 wt% based on the total weight of the
25 milk of lime suspension.

iii) When both preparations are completed, the two are mixed and high-shear stirred for a short time (to limit sulfur-copper reactions) then fed into a spray dryer. During the spray-drying, there is a chemical reaction between copper ammonia complex and calcium polysulfide, likely leading to
30 the formation of molecules of copper sulfide with a portion of unreacted calcium polysulfide. Ammonia is eliminated during the drying process. Part of the chloride counter ions are also present in the final product.

Before the spray drying, the future shell material is mainly made by $\text{Cu}(\text{NH}_3)_4$ and $\text{CuCl}_2/\text{CaS}_x$ in excess compared to the amount of copper. After spray-drying, the shell is mainly made by CuS_5 and CaS_x (the amount remaining from the excess) and $\text{CuCl}_2/\text{Cu}(\text{OH})_2$ (possible traces) as well as CaCl_2 (possible traces).

The invention will now be described by virtue of non-limiting examples.

Examples.-

Example 1.-

About 523 g of a milk of lime according to WO2014/064234 with a solid content of 45% was mixed with 50 g of copper chloride (grade 97% from Alfa Aesar) and 300 ml of ammonia (25% solution from VWR) and stirred at 300 rpm for 3 hours to form the milk of lime suspension n°1.

Calcium polysulfide solution was synthesized using the aforementioned process proposed with a lime/sulfur ratio of 1:1,5 w/w until the water was completely saturated with polysulfide. The sulfur powder (99%) has been bought from VWR Chemicals. The solution was then filtered.

487.5 ml of this saturated calcium polysulfide solution was then mixed with the milk of lime suspension n°1 and spray dried to obtain product 1.

The spray drier was the Atomizer Model MOBILE MINOR, from the Brand GEA. The tank has about a 500 dm^3 capacity, the air pressure can vary between from approximately 0 to 5,5 bar. The injection rate depends on the peristaltic pump used.

The spray drier parameters were as follows:

Mode : counter-current,

Entry pressure : 1 bar,

Entry flow rate : 25 ml/min,

Entry temperature : 210°C

Carbon-sulfur analysis of this product (performed on an Eltra CS 2000 using the prescription of the manufacturer with a high temperature furnace at 1450°C , using 100 mg of product 1 + 100 mg of iron phosphate to

enhance the combustion) showed a total sulfur content of 11%, which was close to our expectation (11-14%).

The sorbent capacity of this product was then evaluated on a mercury bench illustrated on Figure 2.

5 Figure 2 gives a schematic representation of the mercury bench used to evaluate sorbents performances.

The mercury bench 1 used and illustrated in Figure 2 is composed of a few devices connected together. An exhaustive list is given below:

10 -Mercury and flue gas generator (illustrated under number 2) is the bench's central equipment designed to regulate the flow of gases 3, 4, 5, 6 (respectively N_2 , O_2 , HCl and SO_2). It also controls the mercury solution 7 (aqueous solution of diluted $HgCl_2$ in HCl) flow to the evaporator 8 with a peristaltic pump.

15 -Evaporator 8 is an essential device and the start of the circuit, designed to turn the liquid mercury solution 7 into vapor in the gas flow composed at this point of N_2 (illustrated under number 3) and O_2 (illustrated under number 4).

 -Mercury reducing unit 9, 9' is a piece of equipment similar to the evaporator 8, filled with catalyst material to reduce ionic mercury into
20 metallic mercury.

 -The oven (not illustrated) is the reactor 10 heating unit. The temperature inside the reactor 10 is set around 180°C.

 -Reactor 10 is a metallic cylinder of low width. It is plugged to a T connection allowing access to the gas flow and a thermocouple for a precise
25 recording of the temperature inside the reactor 10. It is completed by a 2 μm metallic filter located at the exit of the reactor 10.

 -Bypass 11 is located between the central valves. It helps stabilizing the metallic and ionic mercury levels before the test begins.

 -The Coolers (illustrated under number 12) are dedicated to
30 the elimination of water in the gas flow which is a mandatory operation due to the analyzers 13 sensibility to water. Their temperature is set to 1°C.

-Flow meters 14 are devices used to measure and control the gas flow. Their function is to make sure that the flow is equally divided between the 2 lines.

-Mercury Analyzers (illustrated under number 13) are the
5 analyzers (one on each line) for detecting metallic mercury only in the gas flow after the flow meters. The first one (main line, equipped with Mercury reducing unit 9') shows the concentration of total mercury (as ionic mercury has been reduced just before). The second one shows the concentration of metallic mercury only, which leads to the concentration of ionic mercury by
10 simple subtraction.

The mercury bench was used to measure the mercury removal according to the following experimental procedure:

The tested sorbent is first mixed with purified sand (washed with HCl, triple rinsing with deionized water, size between 125 μm and 250
15 μm) and poured into a fixed bed cylindrical reactor. Then a flue gas having the following composition is injected at a total flow rate of $5.8 \times 10^{-5} \text{ Nm}^3/\text{s}$ so as to cross this bed:

Mercury: $800 \mu\text{g}/\text{Nm}^3$

Sulfur dioxide: 70 ppm

20 Hydrogen chloride: 60 ppm

Dioxygen: 11%

Dinitrogen balance

With two Mercury Analyzers, it is possible to measure both the ionic and the metallic mercury levels at the outlet of the reactor. To achieve
25 that, the gas flow is equally divided in two lanes. Prior to its arrival at the detector/analyzer, the gas flowing in the first lane crosses a mercury reduction unit so as to convert into metallic mercury the possible fraction of mercury present in ionic form. In this way, the totality of the mercury is measured. On the other lane, only the metallic mercury is detected, which
30 enables the calculation of the level of ionic mercury by simple subtraction. With this device, it is possible to evaluate the capacity of mercury reduction

by a solid by applying the principle of the breakthrough curve. The reduction capacity is expressed in ($\mu\text{g Hg}$)/g of solid.

The test starts with a 10-minutes stabilization period, then the gas is redirected through the reactor and the test begins. It ends when the
5 total mercury level ("Hg tot" in figures 3 to 7) is back to its baseline.

From this test, calculations were made by integration of the total mercury curve to access the mercury uptake value, in $\mu\text{g Hg/g}$ of sorbent used. Also, a ratio between the mercury level baseline and the minimum mercury stable level was calculated (maximum removal rate, in %).

10 About 100 mg of product 1 was mixed with 6,5 g of purified sand and poured into the fixed bed reactor. The mercury uptake was found to be 2000 $\mu\text{g/g}$. About 98% of total mercury was removed during the first 15 minutes of the test. The test results are shown Figure 3, where it can be seen that product n°1 shows fast kinetics of mercury capture, allowing product 1 to
15 reach its highest removal rate in seconds. After roughly two hours, mercury is still captured in the gas phase but at a much smaller rate, which is likely caused by a diffusion process of the mercury inside the sorbent particles.

Example 2.-

About 523 g of a milk of lime according to WO2014/064234
20 with a solid content of 45% was mixed with 12,5 g of copper chloride (grade 97% from Alfa Aesar) and 75 ml of ammonia (25% solution from VWR) and stirred at 300 rpm for 3 hours to form the milk of lime suspension n°2.

Calcium polysulfide solution was synthesized using the aforementioned process proposed with a lime/sulfur ratio of 1:1,5 w/w until
25 the water was completely saturated with polysulfide. The sulfur powder (99%) has been bought from VWR Chemicals. The solution was then filtered.

About 122 ml of this saturated calcium polysulfide solution was then mixed with the milk of lime suspension n°2 and spray dried to obtain product 2.

30 The sorbent capacity of this product was then evaluated on a mercury bench according to the experimental procedure disclosed in example 1.

About 100 mg of product 2 was mixed with 6,5 g of purified sand and poured into the fixed bed reactor. The mercury uptake value was found to be 850 µg/g. About 95% of total mercury was removed during the first 5 minutes of the test.

5 The test results are shown in Figure 4 where it can be seen that product n°2 has a similar behavior compared to product 1 during the first 15 minutes of the test. After this period of time, the gap between the total mercury value detected and the baseline is much smaller and is reducing faster than for product 1, showing therefore limited diffusion due to the
10 thinner shell layer of sulfur. The total uptake is interesting (850 µg/g vs 2000 µg/g, with 4 times less copper and sulfur).

Comparative example 1.-

The sorbent capacity of activated carbon according to prior art was also evaluated on the same mercury bench and according to the same
15 experimental procedure as disclosed in example 1.

For this test, about 50 mg of commercial product Darco Hg-LH was mixed with 6,5 g of purified sand and poured into the fixed bed reactor.

The mercury uptake value was found to be 8000 µg/g. About 95% of total mercury was removed during 70 minutes, after a 1-hour period of
20 stabilization.

The test results are shown Figure 5 where it can be seen that, as expected, activated carbons have great mercury uptake values, with however slower kinetics, as it takes almost 1 hour to reach the maximum removal rate. No stabilization of the total mercury level under the baseline
25 was observed, which means that no diffusion is encountered, probably because of the highly porous structure of activated carbon and good accessibility of those pores.

Comparative example 2.-

About 10 g of bentonite was mixed with 7,8 g of copper
30 chloride and 40 ml of ammonia and stirred at 300 rpm for 5 hours. The slurry was then filtered using a Buchner filter. The solid phase was then mixed with a solution of 20,65 g Na₂S in 100 ml H₂O and stirred for 5 hours. After a second

Buchner filtration, the solid phase was dried overnight to obtain a copper sulfide-impregnated bentonite sample.

The sorbent capacity of this product was then evaluated on a mercury bench according to the experimental procedure disclosed in example 1.

About 100 mg of copper sulfide-impregnated bentonite was mixed with 6,5 g of purified sand and poured into the fixed bed reactor. The mercury uptake value was found to be 100 $\mu\text{g/g}$. About 80 % of total mercury was removed during the first 5 minutes of the test.

The test results are shown in Figure 6, where it can be seen that bentonite, which is known as a good cation exchanger, helps copper being accessible and has a good mercury oxidation capacity but the resulting total mercury uptake is weak.

Comparative example 3.-

About 625 g of Ludox HS-40 (colloidal silica available from Sigma-Aldrich, solid content 40%) was mixed with 50 g of copper chloride and 300 ml of ammonia (25% solution) in 2 kg of deionized water and stirred for 3 hours at 300 rpm so as to form a suspension of colloidal silica.

Calcium polysulfide solution was synthesized using the process proposed with a lime/sulfur ratio of 1:1,5 w/w until the water was completely saturated with polysulfide. The solution was then filtered.

600 ml of this saturated calcium polysulfide solution were then mixed with said suspension of colloidal silica and spray dried to obtain the spray dried colloidal silica product.

The sorbent capacity of this product was then evaluated on a mercury bench according to the experimental procedure disclosed in example 1.

About 100 mg of spray dried colloidal silica was mixed with 6,5 g of purified sand and poured into the fixed bed reactor.

The mercury uptake value was found to be 500 $\mu\text{g/g}$. About 93 % of total mercury was removed during the first 15 minutes of the test.

The test results are shown in Figure 7, where it can be seen that the spray dried colloidal silica sample has good kinetics and removal rate, but weak total mercury uptake compared with product 1 due to the amount of impregnant trapped between colloidal silica particles in the core of the
5 sorbent.

It should be understood that the present invention is not limited to the described embodiments and that variations can be applied without going outside of the scope of the appended claims.

« CLAIMS »

1. Lime-based sorbent composition containing particles for removing heavy metals, in particular mercury, from flue gases, said particles being core-shell particles characterized in that the core comprises a calcium-magnesium compound fitting the formula
5 $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.u\text{I}$, wherein I represents impurities, a, b, x, y, z and t each being mass fractions ≥ 0 and $\leq 100\%$, u being mass fraction ≥ 0 and $\leq 20\%$ by weight, based on the total weight of said at least one calcium-magnesium compound, characterized in that said core is coated with a shell presenting a thickness of less than $20\text{ }\mu\text{m}$ and more than
10 50 nm , shielding the core from the flue gases medium and comprising at least a metal salt and a sulfur-based compound.

2. Lime-based sorbent composition according to claim 1, wherein said sulfur-based compound is fitting the formula $\text{A}_\alpha\text{S}_\beta\text{O}_\gamma$ wherein α , β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group
15 consisting of calcium, magnesium, potassium, sodium and their mixture.

3. Lime-based sorbent composition according to claim 1 or claim 2, wherein said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as
20 calcium polysulfide, and their mixture.

4. Lime-based sorbent composition according to anyone of the claims 1 to 3, wherein said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.

25 5. Lime-based sorbent composition according to anyone of the claims 1 to 4, wherein said metal salt is a copper halide, preferably a copper chloride.

6. Lime-based sorbent composition according to anyone of the claims 1 to 5, further comprising a doping agent chosen in the group

consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.

7. Lime-based sorbent composition according to anyone of
5 the claims 1 to 6, further comprising a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docetyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and their mixtures.

10 8. Lime-based sorbent composition according to anyone of the claims 1 to 7, wherein $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium-magnesium compound.

9. Lime-based sorbent composition according to anyone of
15 the claims 1 to 8, wherein the calcium-magnesium compound presents a particle size distribution wherein d_{10} is comprised in the range from 0,5 to 3 μm , preferably from 0,75 to 2 μm ; d_{90} is comprised in the range from 7 to 50 μm , preferably from 10 to 40 μm , d_{50} is comprised in the range from 3 to 50 μm , preferably from 4 to 30 μm .

20 10. Lime-based sorbent composition according to anyone of the claims 1 to 9, wherein said shell presents a thickness of less than 10 μm , preferably less than 5 μm , in particular less than 2 μm , and greater than 100 nm, preferably greater than 200 nm, in particular greater than 300 nm.

11. Lime-based sorbent composition according to anyone of
25 the preceding claims, wherein the ratio between calcium-magnesium compound and sulfur ranges from 15:1 w/w to 1:1 w/w and preferably is of 2,5:1 w/w.

12. Lime-based sorbent composition according to anyone of
the preceding claims, wherein the ratio between calcium-magnesium
30 compound and said metal salt ranges from 15:1 w/w and 1:1 w/w and preferably is of 5:1 w/w.

13. Process to produce a lime-based sorbent composition comprising the steps of :

i) Mixing a metal ammonia complex with an aqueous suspension of calcium-magnesium compound fitting the formula
5 $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO}.y\text{MgO}.z\text{Ca}(\text{OH})_2.t\text{Mg}(\text{OH})_2.ul$, wherein l represents impurities, a , b , x , y and u each being mass fractions ≥ 0 and $\leq 50\%$, z and t each being mass fractions ≥ 0 and $\leq 100\%$ by weight, based on the total weight of said at least one calcium-magnesium compound, for a predetermined first period of time sufficient to ensure complete dispersion of
10 metal on the calcium-magnesium particles, to form a suspension of calcium-magnesium particles onto which said metal is dispersed,

ii) Mixing said suspension of calcium-magnesium particles onto which said metal is dispersed with a calcium-magnesium polysulfide solution for a second predetermined period of time to form a lime-based
15 composition pre-mix,

iii) Feeding said lime-based composition pre-mix into a spray-dryer to form a spray dried lime-based composition presenting particles being core-shell particles, wherein the core comprises said calcium-magnesium compound, said core being further coated with a shell
20 presenting a thickness of more than 50 nm and less than $20\mu\text{m}$, shielding the core from the flue gases medium and comprising at least a metal salt and a sulfur-based compound.

14. Process according to claim 13, wherein said aqueous suspension of calcium-magnesium compound presents a solid content
25 between 30 and 45 w% with respect to the total weight of the aqueous suspension of calcium-magnesium compound.

15. Process according to claim 13 or 14, wherein the aqueous suspension of calcium-magnesium compound comprises particles having a particle size distribution wherein d_{50} is comprised in the range from
30 $0,5$ to $20\mu\text{m}$, preferably from $0,5$ to $10\mu\text{m}$ and more preferably from 1 to $2,5\mu\text{m}$.

16. Process according to anyone of the claims 13 to 15, wherein said sulfur-based compound is fitting the formula $A_{\alpha}S_{\beta}O_{\gamma}$ wherein α , β and γ each being mass fraction with $\beta \neq 0$ and where A is chosen in the group consisting of calcium, magnesium, potassium, sodium and their mixture.
- 5 17. Process according to anyone of the claims 13 to 16, wherein said sulfur-based compound is chosen in the group consisting of sulfide salts, such as calcium sulfide, dithiocarbamates, sulfate salts, such as calcium sulfate, polymer-based dithiocarbamates, polysulfide salts, such as calcium polysulfide, and their mixture.
- 10 18. Process according to anyone of the claims 13 to 17, wherein said metal salt is chosen in the group consisting of salts of titanium, vanadium, manganese, iron, nickel, copper, zinc, and their mixture, preferably copper.
- 15 19. Process according to anyone of the claims 13 to 18, wherein said metal salt is a copper halide, preferably a copper chloride.
- 20 20. Process according to anyone of the claims 13 to 19, further comprising a step of adding a doping agent chosen in the group consisting of alkali metal halides, such as sodium or potassium halides, alkali earth metal halides, such as calcium or magnesium halides, ammonium halides and their mixtures.
21. Process according to claim 20 wherein said doping agent is added to the calcium-magnesium polysulfide solution.
22. Process according to claim 20 wherein said doping agent is added to the spray dried lime-based composition.
- 25 23. Process according to anyone of the claims 13 to 22, further comprising a step of adding a dispersing agent chosen in the group consisting of (poly)sulfates, such as sodium docetyl sulfate (SDS), (poly)sulfonates, (poly)phosphates, (poly)phosphonates, such as diethylenetriamine-penta(methylene phosphonic acid) (DTPMP), polyols, and
30 their mixtures to the aqueous suspension of calcium-magnesium compound fitting the formula $aCaCO_3.bMgCO_3.xCaO.yMgO.zCa(OH)_2.tMg(OH)_2.ul$.

24. Process according to anyone of the claims 13 to 23, wherein in the calcium-magnesium compound fitting the formula $a\text{CaCO}_3.b\text{MgCO}_3.x\text{CaO.yMgO.zCa(OH)}_2.t\text{Mg(OH)}_2.ul$, $z + t \geq 60\%$, preferentially $\geq 70\%$, preferably $\geq 80\%$, more preferably $\geq 90\%$, in particular $\geq 93\%$ by weight, based on the total weight of said at least one calcium magnesium compound.

25. Process according to anyone of the claims 13 to 24, wherein said shell presents a thickness of less than $10\text{ }\mu\text{m}$, preferably less than $5\text{ }\mu\text{m}$, in particular less than $2\text{ }\mu\text{m}$, and greater than 100 nm , preferably greater than 200 nm , in particular greater than 300 nm .

26. Process according to anyone of the claims 13 to 25, wherein the ratio between calcium-magnesium compound and sulfur ranges from $1:1\text{ w/w}$ to $1:2\text{ w/w}$, preferably of $1:1,5\text{ w/w}$ in the calcium-magnesium polysulfide composition.

27. Process according to anyone of the claims 13 to 26, wherein the ratio between said calcium-magnesium compound and said metal salt ranges from $15:1\text{ w/w}$ to $1:1\text{ w/w}$, preferably is of $5:1\text{ w/w}$ in the suspension of calcium-magnesium particles onto which the metal is dispersed.



Fig. 1

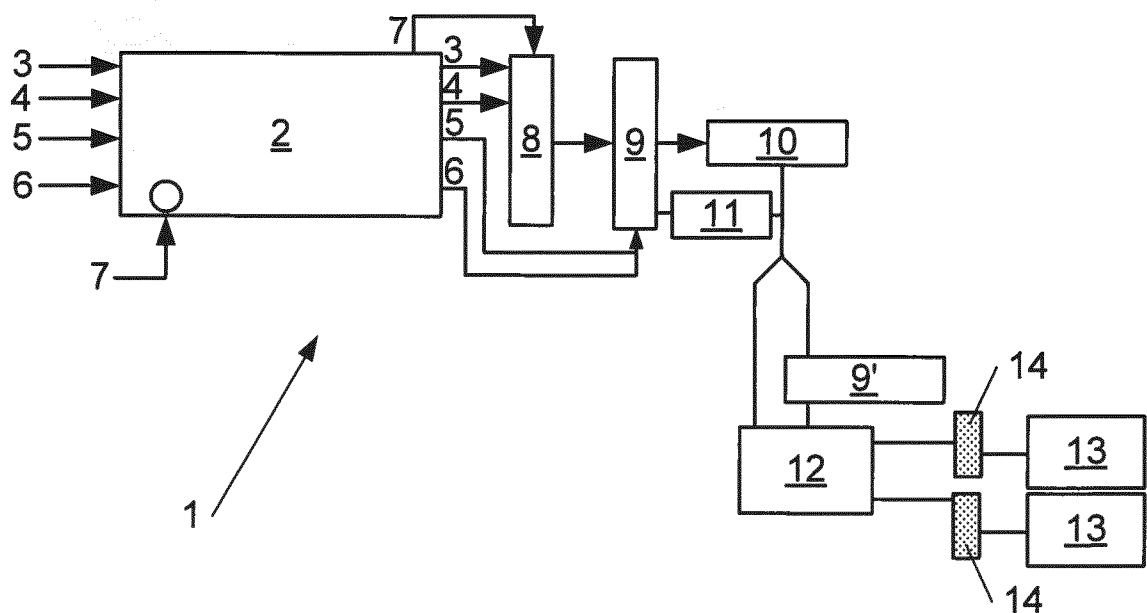
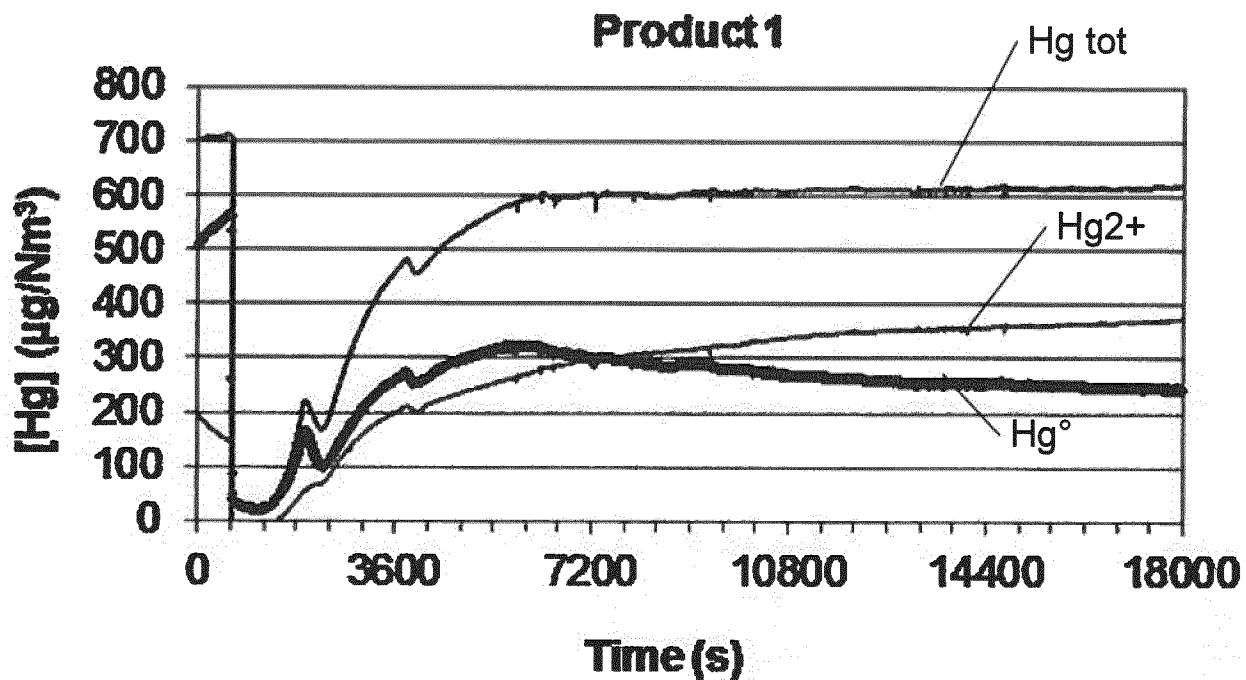
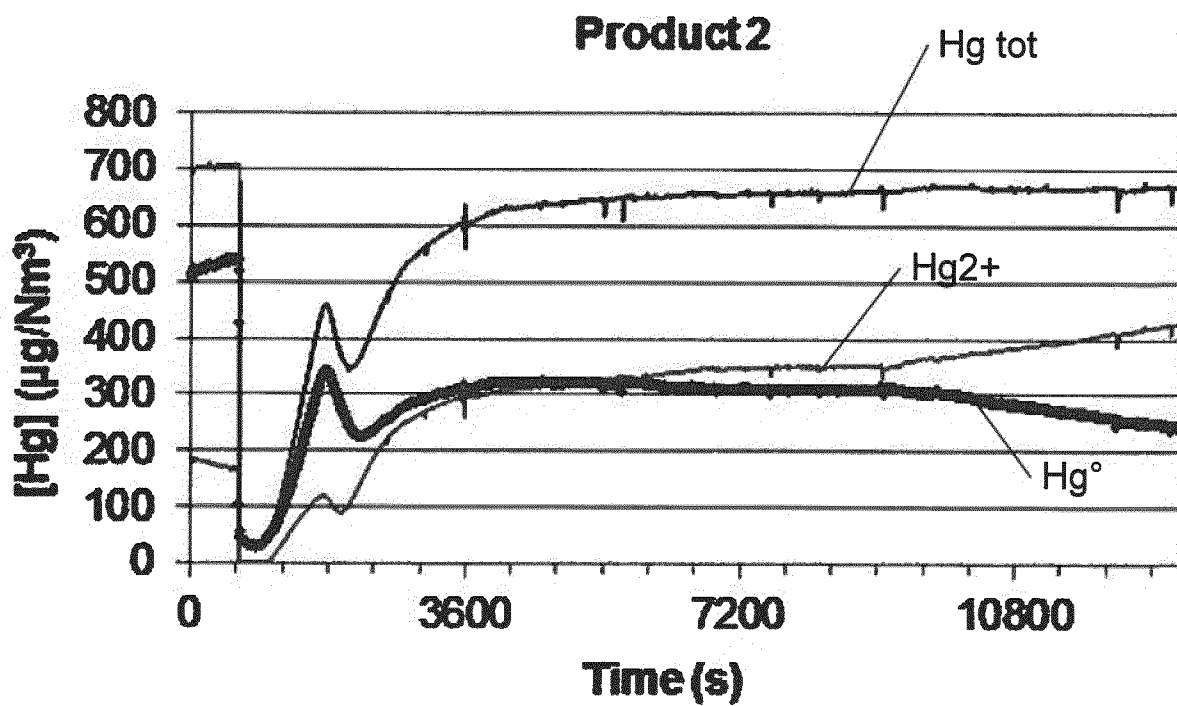
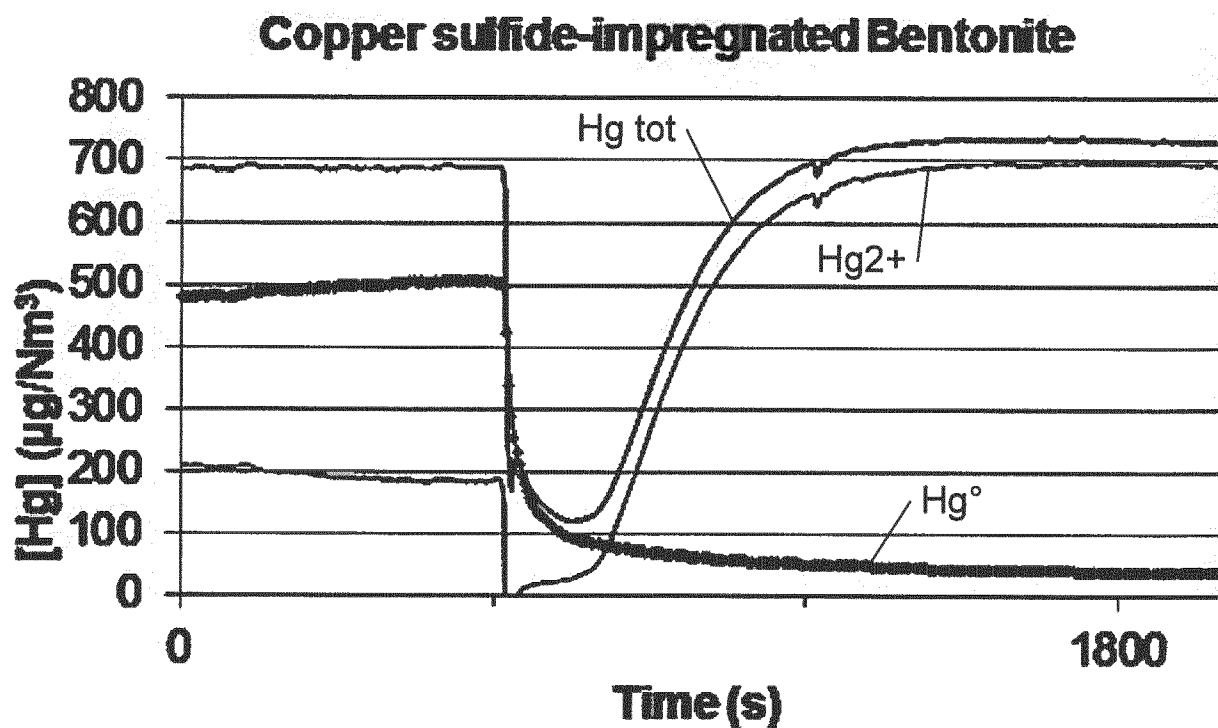
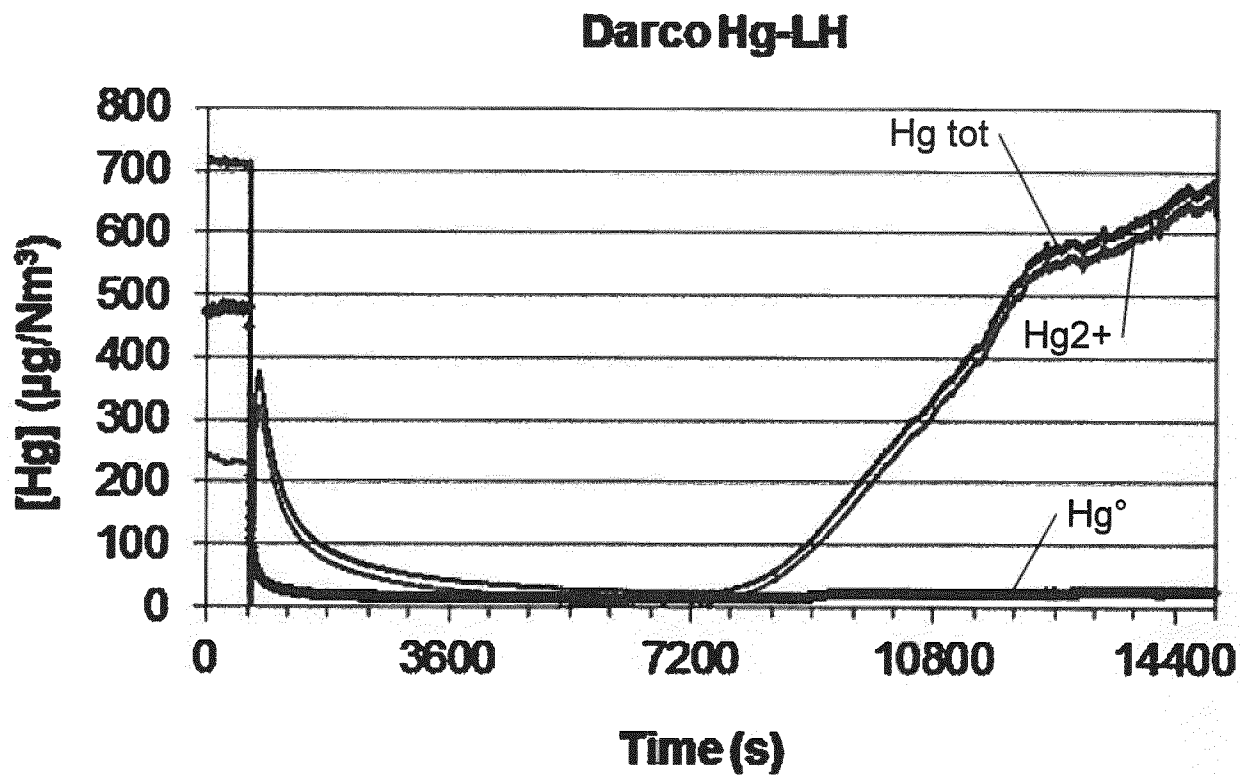


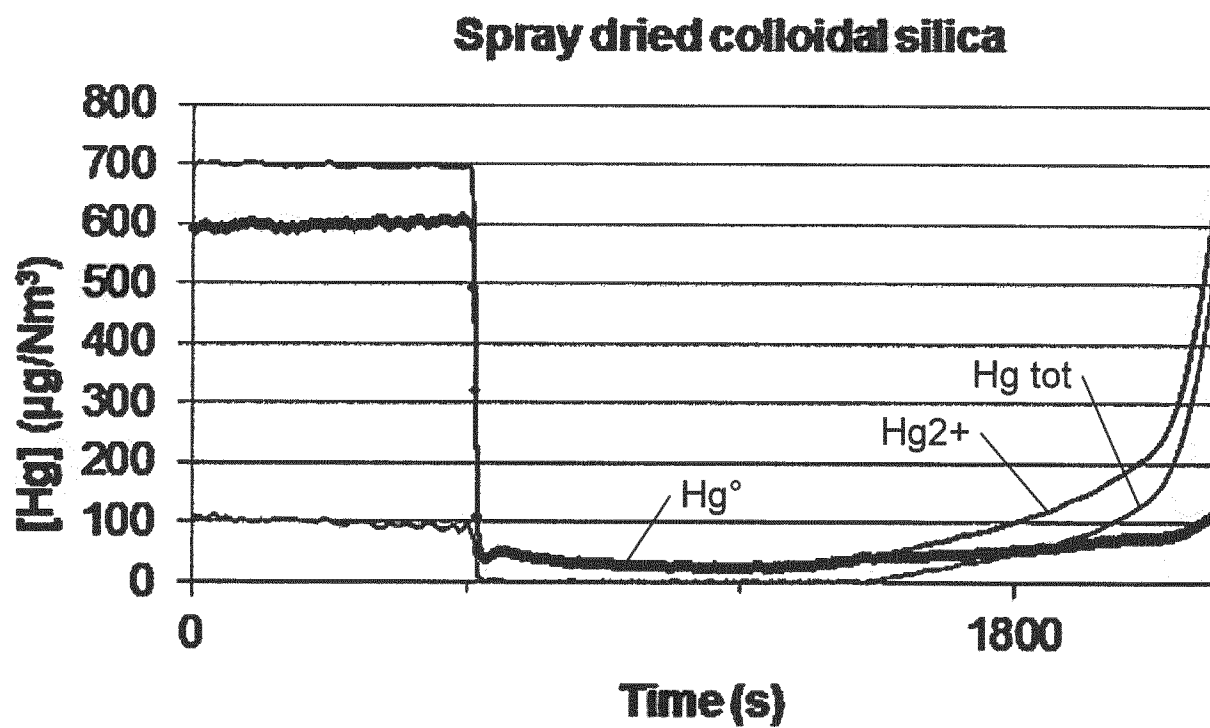
Fig. 2

**Fig. 3****Fig. 4**

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4/4

***Fig. 7***

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/061147

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/04 B01J20/32 B01J20/02 B01J20/28
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/089479 A1 (ERLANG NICHOLAS S [US] ET AL) 11 April 2013 (2013-04-11)	1-12
A	paragraph [0101] paragraph [0103] - paragraph [0115]; examples 1-4 paragraph [0059] - paragraph [0060] paragraph [0068] - paragraph [0069] -----	13-27
A	US 2011/123422 A1 (WANG ZHEN [US]) 26 May 2011 (2011-05-26) the whole document -----	1-27
A	US 2002/035925 A1 (EL-SHOUBARY YOUSSEF [US] ET AL) 28 March 2002 (2002-03-28) the whole document -----	1-27



Further documents are listed in the continuation of Box C.



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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/061147

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013089479 A1	11-04-2013	US 2013089479 A1	11-04-2013
		US 2014084209 A1	27-03-2014
		WO 2013052876 A1	11-04-2013

US 2011123422 A1	26-05-2011	AU 2011357684 A1	27-06-2013
		CA 2820097 A1	09-08-2012
		CN 103313770 A	18-09-2013
		EP 2670510 A1	11-12-2013
		EP 2870990 A1	13-05-2015
		JP 2014508638 A	10-04-2014
		KR 20130141591 A	26-12-2013
		US 2011123422 A1	26-05-2011
		WO 2012106007 A1	09-08-2012

US 2002035925 A1	28-03-2002	NONE	
