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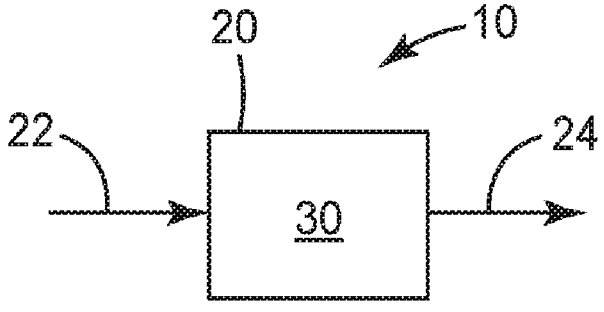


FIG. 1

(57) Abstract: A filter media composition includes a ferrihydrite material having an average pore size (BJH) in a range from 1 to 3 nm and a surface area (BET) of at least 200 m^2/g or at least 250 m^2/g or at least 300 m^2/g.

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FILTER MEDIA FOR RESPIRATORY PROTECTION

BACKGROUND

Sorbents used in respiratory filter cartridges are typically based upon activated carbon. An attribute of activated carbon is its ability to adsorb organic vapors (OV). Activated carbons, although high in surface area, are generally unable to adsorb low boiling point polar compounds such as ammonia, thus some type of impregnant is used to react and trap the contaminant.

In order to filter other contaminant gases ('hazardous' gases, e.g. acidic gases, ammonia, cyanides, aldehydes), chemicals are added to the activated carbon in a process known as impregnation. For example, the Lewis acidic transition metal salt $ZnCl_2$ is added to carbon to produce a sorbent for ammonia removal. Impregnation of any support (e.g., activated carbon) involves a balance of loading a sufficient amount of the reactive impregnant without destroying the high surface area of the support.

When considering inorganic materials as sorbent components, factors such as toxicity, stability under relevant conditions, and cost represent key attributes. Traditional carbon impregnants based upon copper and zinc are often oxides in the 2+ oxidation state, formed via thermolysis (at ca. 180-200°C) of activated carbons treated with Cu and/or Zn salts that are soluble in aqueous or ammoniacal solutions. These inorganic materials alone, however, each commonly suffer from low porosity and surface area.

There are over a dozen known iron oxides including hydrated and hydroxide-containing materials. Generally, these compounds exist in nature and may also be synthesized in a laboratory. Iron oxides with high porosity and surface area are usually prepared using non-aqueous solvents, templating reagents, and high calcination temperatures. A naturally occurring iron oxide mineral known as 'two-line' ferrihydrite (henceforth referred to as ferrihydrite) is composed of nanocrystalline aggregates and is characterized by two poorly defined, broadened maxima in x-ray diffraction (XRD) methods.

SUMMARY

The present disclosure relates to filter media for respiratory protection. In particular the filter media is an unsupported ferrihydrite material that is capable of removing hazardous gases from a respiratory airstream. The ferrihydrite material can be prepared using low temperature, aqueous based processes and can be a doped material.

In one aspect, a composition includes a doped ferrihydrite material having an average pore size (BJH) in a range from 1 to 3 nm and a surface area (BET) of at least 200 m^2/g or at least 250 m^2/g or at least 300 m^2/g.

In another aspect, a respiratory protection filter includes a housing having an air stream inlet and an air stream outlet and containing an amount of filtration media in fluid connection and between the air stream inlet and the air stream outlet. The filtration media includes free-standing granular doped ferrihydrite material.

In a further aspect, a method includes combining a hydrated iron (III) salt with a metal dopant salt to form a mixture and blending a bicarbonate material with the mixture to form a wet doped ferrihydrite material and salt co-product. Then the method includes drying the wet doped ferrihydrite material and salt co-product to a moisture content of less than 10% by wt or less than 5% by wt to form a dried doped ferrihydrite material and salt co-product. Then, washing away the salt co-product with water to form a wet doped ferrihydrite material and drying the wet doped ferrihydrite material to a moisture content of less than 10% by wt or less than 5% by wt to form a dried doped ferrihydrite material.

These and various other features and advantages will be apparent from a reading of the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings, in which:

FIG. 1 is a schematic drawing of an illustrative respiratory protection filter; and

FIG. 2 is a flow diagram of an illustrative method.

DETAILED DESCRIPTION

In the following detailed description, reference is made to the accompanying drawings that form a part hereof, and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present disclosure. The following detailed description, therefore, is not to be taken in a limiting sense.

All scientific and technical terms used herein have meanings commonly used in the art unless otherwise specified. The definitions provided herein are to facilitate understanding of certain terms used frequently herein and are not meant to limit the scope of the present disclosure.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical

parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the properties desired by those skilled in the art utilizing the teachings disclosed herein.

The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

As used in this specification and the appended claims, the singular forms "a", "an", and "the" encompass embodiments having plural referents, unless the content clearly dictates otherwise.

As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

As used herein, "have", "having", "include", "including", "comprise", "comprising" or the like are used in their open ended sense, and generally mean "including, but not limited to". It will be understood that "consisting essentially of", "consisting of", and the like are subsumed in "comprising," and the like.

The term "free-standing" material refers to an unsupported material or a material that is not impregnated onto a support material.

The present disclosure relates to filter media for respiratory protection. In particular the filter media is an unsupported ferrihydrite material that is capable of removing reactive gases from a respiratory airstream. The ferrihydrite material can be formed using low temperature, aqueous based processes and can be a doped material. The ferrihydrite material has an average pore size in a range from 1 to 3 nm (BJH method) and a surface area of at least 200 m^2/g or at least 250 m^2/g or at least 300 m^2/g (BET method). Filtration media within a respiratory protection filter has at least 20% by wt, or at least 30% by wt, or at least 50% by wt ferrihydrite material. The ferrihydrite material can be formed at temperatures below 115 degrees centigrade or below 110 degrees centigrade. Forming the ferrihydrite material includes at least one drying step that removes only water or moisture. The ferrihydrite material is granulated to a mesh size in a range from 12 to 50 U.S. standard sieve series. While the present disclosure is not so limited, an appreciation of various aspects of the disclosure will be gained through a discussion of the examples provided below.

FIG. 1 is a schematic drawing of an illustrative respiratory protection filter **10**. The respiratory protection filter **10** includes a housing **20** having an air stream inlet **22** and an air stream outlet **24** and containing an amount of filtration media **30** in fluid connection and between the air stream inlet **22** and the air stream outlet **24**. The filtration media **30** includes free-standing granular doped ferrihydrite material. In many embodiments, the filtration media **30** includes at

least 20% wt or at least 30% wt or at least 50% wt ferrihydrite material or doped ferrihydrite material.

The filtration media **30** can include one or more additional types of filtration material, such as, activated carbon, for example. The ferrihydrite material is not impregnated onto a support material, such as activated carbon, for example.

The ferrihydrite material is capable of removing hazardous gas from an air stream passing through the filtration media **30** at ambient conditions or atmospheric pressure and -20 to 40 degrees centigrade and 5% to 95% relative humidity. These hazardous gases include both acidic and basic gases.

The ferrihydrite material described herein has an average pore size (BJH method) in a range from 1 to 3 nm and a surface area (BET) of at least 200 m^2/g or at least 250 m^2/g or at least 300 m^2/g. The doped ferrihydrite material has a molar ratio of iron:dopant in a range from 95:5 to 75:25 or from 90:10 to 80:20.

The ferrihydrite material can be doped with a dopant material comprising a metal such as Cu, Zn, Ca, Ti, Mg, Zr, Mn, Al, Si, Mo, Ag or mixtures thereof forming a doped ferrihydrite material. Dopants may be secondary metal oxides that are incorporated into the iron oxide for beneficial effect. In many embodiments, the doped ferrihydrite material includes Cu, Zn and/or Mn as dopant materials. The doped ferrihydrite material has a moisture content of less than 10% by wt or less than 5% by wt.

The ferrihydrite material forms a powder material that defines aggregate particles having a median largest lateral dimension in a range from 1 to 100 micrometers or from 15 to 45 micrometers or from 20 to 40 micrometers or about 30 micrometers. These particles are granulated to define granules having a mesh size in a range from 12 to 50 or from 20 to 40. Any useful granulation process can be utilized. In many embodiments, the granules are formed with compression and without the use of a binder. The ferrihydrite granules have a moisture content of less than 10% wt or less than 5% wt.

FIG. 2 is a flow diagram of an illustrative method **100**. The method includes combining a hydrated iron (III) salt with a metal dopant salt to form a mixture (powder mixture) at block **110** and blending a bicarbonate material (preferably a powder sodium bicarbonate) with the mixture to form a wet doped ferrihydrite material and salt co-product at block **120**. Then drying the wet doped ferrihydrite material and salt co-product to a moisture content of less than 10% by wt or less than 5% by wt to form a dried doped ferrihydrite material and salt co-product at block **130**. The salt co-product is washed away to form a wet doped ferrihydrite material at block **140**. The wet doped ferrihydrite material is dried to a moisture content of less than 10% by wt or less than 5% by wt to form a dried doped ferrihydrite material at block **150**. The doped ferrihydrite

material at block **160** is then granulated to form a granulated filtration media product at block **170**.

The method **100** occurs at relatively low temperatures. In many embodiments the method **100** has a processing temperature for all the steps that is no greater than 115 degrees centigrade or no greater than 110 degrees centigrade. In many embodiments, the drying steps **130, 150** removes only water or moisture from the wet doped ferrihydrite material and salt co-product or the wet doped ferrihydrite material.

A general illustrative procedure for the preparation of the doped ferrihydrite material described herein involves:

(i) The combination and mixing of solid $Fe(NO_3)_3 \cdot 9H_2O$ and another metal salt (e.g. Cu, Zn, Mn, Al) in an appropriate stoichiometric ratio, in a mixing vessel. The powders are mixed so that they appear to be a free-flowing (e.g., no obvious lumps) powder and relatively homogeneous.

(ii) The addition of free-flowing bicarbonate powder in an appropriate ratio.

(iii) The resulting powder mixture is then ground together either manually or with mechanical stirring to mix the reagents. This mixture becomes frothy (CO_2 evolution and water release) over the course of the reaction and gradually darkens to a red-orange slurry. Mixing continues until gas evolution ceases. After this time period the stirred mixture thickens to a solid brownish solid.

(iv) The resulting brown material is placed in an oven at 100-105°C for a period of time to dry to less than 10% by wt water. After this time period, nitrate salts and possible other co-products are observed in the dried material.

(v) The solid is then transferred to a filtration apparatus and washed with an appropriate amount of water to rid the solid of water-soluble salt co-products.

(vi) The washed material is placed in an oven at 100-105°C for a period of time to dry to less than 10% by wt or less than 5% by wt water. This product has a brownish color.

An additional procedure for the preparation of doped ferrihydrite material involves the precipitation of iron and secondary metal salts dissolved together in an aqueous solution. This is accomplished by raising the pH of the acidic metal salt solution to pH 7-8 by the addition of a base, as described in Example 6 below. This method may form more heavily aggregated materials than Examples 1-5, resulting in larger particle sizes as reported in Table 2.

Objects and advantages of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

Examples

All parts, percentages, ratios, etc. in the examples are by weight, unless noted otherwise. Solvents and other reagents used are obtained from Sigma-Aldrich Corp., St. Louis, Missouri unless specified differently.

Material Listing

Unless otherwise indicated, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot 2.5H_2O$, $CuSO_4 \cdot 5H_2O$, NaOH, NH_4HCO_3, and $NaHCO_3$ were obtained in reagent grade from Sigma-Aldrich Co. (St. Louis, MO, USA).

Example 1

Un-doped ferrihydrite was prepared according to the procedure given in Inorg. Chem. **51** (2012) 6421. In summary, 0.05 mol $Fe(NO_3)_3 \cdot 9H_2O$ was combined with 0.15 mol of NH_4HCO_3 for 30 minutes in a mortar and pestle. After drying the resulting product for 14 hours at 100°C in a muffle furnace under static air, the material was washed with three 50 mL portions of deionized water using a 5 cm diameter Buchner funnel and vacuum filter apparatus equipped with Fisherbrand filter paper (medium porosity, Grade P5). The filtered solid was then dried at 100°C for 14 hours to a moisture content of less than 5 wt. %. The resulting material was then formed into pellets using a 13 mm die and Carver press using a pressure of 70000 PSI. The pellets were then crushed and sized to 20 x 40 mesh granules.

Example 2

Un-doped ferrihydrite was prepared using a similar procedure to Example 1, with the exception that $NaHCO_3$ was used instead of NH_4HCO_3. $NaHCO_3$ was added to pre-ground $Fe(NO_3)_3 \cdot 9H_2O$ with stirring over the course of approximately 30 seconds. The powder mixture became reddish orange and carbon dioxide gas evolution was noticed during stirring over the course of the first few minutes. Manual stirring with the pestle was continued for approximately 25 minutes until the dark brown slurry hardened and gas evolution was no longer noticeable. The solid mixture was then dried and placed in an oven set at 100°C. After 14 hours, the dried solid appeared to have a white powder coating on top of the clumped material. The solid was filtered, washed and dried and formed into granules in an analogous fashion to Example 1.

Example 3

Copper-doped ferrihydrite was prepared with an initial Cu:Fe molar ratio of 1:9. The pre-ground powders $Fe(NO_3)_3 \cdot 9H_2O$ (909 g, 2.25 mol), $Cu(NO_3)_2 \cdot 2.5H_2O$ (59.7 g, 0.25 mol) and $NaHCO_3$ (609 g, 7.25 mol) were weighed into separate containers. The copper(II) nitrate was

then combined with the iron(III) nitrate in a 4L stainless steel bowl and the powders were mixed intimately for several minutes with a pestle. After addition of the sodium bicarbonate, the powder mixture became reddish orange and carbon dioxide gas evolution was noticed during stirring over the course of the first few minutes. Manual stirring with the pestle was continued for approximately 45 minutes until the dark brown slurry hardened and gas evolution was no longer noticeable. The solid mixture was then dried and placed in a forced air oven set at 100°C for 14 hours, after which time the dried solid appeared to have a white powder coating on top of the clumped material. The solid was then transferred to an 11cm diameter Buchner funnel fitted with Fisherbrand filter paper (coarse porosity, Grade P8). After attachment of the funnel to a vacuum filtration flask, the solid was washed with deionized water (3.5 L in 500 mL portions). The solid was filtered and dried to a moisture content of less than 5 wt. % and formed into granules in an analogous fashion to Example 1.

Example 4

Copper-doped ferrihydrite was prepared with an initial Cu:Fe molar ratio of 1:4 in an analogous procedure to Example 3, with the exception that NH_4HCO_3 was used in place of $NaHCO_3$. After the first drying step, the dried solid appeared to have some bluish-white crystals deposited on the top surface. Instead of a colorless wash as observed in Example 3, a bluish colored filtrate was observed for the first 2 L of wash water used. The filtered solid was dried to a moisture content of less than 5 wt. % and formed into granules in an analogous fashion to Example 1.

Example 5

Zinc-doped ferrihydrite was prepared with an initial Zn:Fe molar ratio of 1:4 in an analogous procedure that led to Example 4, with the exception that $Zn(NO_3)_2 \cdot 6H_2O$ was used in place of $Cu(NO_3)_2 \cdot 2.5H_2O$, and 6.75 mol of NH_4HCO_3 was used instead of 7.25 mol. Instead of a blue wash as observed in Example 4, an orange colored wash was observed. The filtered solid was dried to a moisture content of less than 5 wt. % and formed into granules in an analogous fashion to Example 1.

Example 6

Copper-doped ferrihydrite was prepared with an initial Cu:Fe ratio of 1:9. A solution of $Fe_2(SO_4)_3 \cdot 2.5H_2O$ (50.6g, 0.10 mol) was prepared in 500 mL deionized water. A separate solution of $CuSO_4 \cdot 5H_2O$ (5.74g, 0.023 mol) was prepared in 500 mL deionized water. These solutions were then added to a 2000 mL beaker and stirred magnetically. After 5-10 minutes of mixing, 3.0 mol/L NaOH solution was added dropwise using a MasterFlex© peristaltic pump at

a flow rate of approximately 3.4 mL/min. The flow of NaOH was terminated after 227 mL was added and the pH of the reaction mixture was approximately 7. The mixture was left to stir for 1.5 hours after the base addition was complete. Stirring was then stopped and the mixture was left to settle overnight for 16 hours. A major portion (approximately 70% by reaction mixture volume) of the resulting supernatant was decanted from the beaker, and the remaining contents were then transferred to an 11cm diameter Buchner funnel fitted with Fisherbrand filter paper (coarse porosity, Grade P8). After attachment of the funnel to a vacuum filtration flask, the solid was washed with deionized water (750 mL in 250 mL portions). The solid was filtered and dried to a moisture content of less than 10 wt. %. The dried material was crushed and sized to 20 x 40 mesh granules.

Testing Methods

Tube Testing

A tube testing apparatus was used for breakthrough testing. The sample tubes employed are composed of polyvinylchloride (PVC) (inner diameter = 6.5mm) with a fine stainless steel mesh near the base. These tubes are loaded with a specified volume of filter media granules for testing and are packed to a constant volume by repeatedly tapping the lower end against a hard surface. The sample tube is connected to flexible Teflon tubing using ultra-torr (Swagelok) fittings. Challenge gases of desired concentrations are then delivered through the vertical tube through the top (inlet) portion of the tube at a specified flow rate and the effluent gas that exits the sorbent bed through the lower end of the tube (outlet) is then transported to a detector for analysis.

SO_2 Breakthrough Testing:

A sample of filter media granules, either obtained from a commercial vendor or prepared according to a given example, equating to a volume of either 1 or 1.7 cc was transferred to the tube testing apparatus outlined above and weighed. In this case the outlet gas stream was analyzed by a MIRAN SapphIRe IR portable air analyzer. The filter media granules were "tapped" until no significant reduction in volume was observed by the human eye. The sample in the tube was then exposed to a test stream of approximately 200mL/minute of conditioned air (<15% RH) that contained about 1000 ppm of sulfur dioxide (SO_2) in air from a certified gas mixture from Linde (Whitby, ON, Canada). The air downstream from the filter media granules was monitored for breakthrough using a MIRAN SapphIRe IR portable air analyzer. The breakthrough time was defined as the time at which a concentration of 20 ppm was observed downstream from the sample.

NH_3 Breakthrough Testing:

A sample of filter media granules, either obtained from a commercial vendor or prepared according to a given example, equating to a volume of either 1 or 1.7 cc was transferred to the tube testing apparatus outlined above and weighed. In this case the outlet gas stream was analyzed by a MIRAN SapphIRe IR portable air analyzer. The filter media granules were "tapped" until no significant reduction in volume was observed by the human eye. The sample in the tube was then exposed to a test stream of approximately 200mL/minute of conditioned air (<15% RH) that contained about 1000 ppm of ammonia (NH_3) in air from a certified gas mixture from Linde (Whitby, ON, Canada). The air downstream from the filter media granules was monitored for breakthrough using a MIRAN SapphIRe IR portable air analyzer. The breakthrough time was defined as the time at which a concentration of 20 ppm was observed downstream from the sample.

HCN Breakthrough Testing:

A sample of filter media granules, either obtained from a commercial vendor or prepared according to a given example, equating to a volume of 1.7 cc was transferred to the tube testing apparatus outlined above and weighed. In this case the outlet gas stream was analyzed by a gas chromatograph with a flame ionization detector (GC-FID). The filter media granules were "tapped" until no significant reduction in volume was observed by the human eye. The sample in the tube was then exposed to a test stream of approximately 260mL/minute of conditioned air (<15% RH) that contained about 2000 ppm of hydrogen cyanide (HCN). The air downstream from the filter media granules was monitored for breakthrough using a GC-FID system for both HCN, the challenge gas, and cyanogen (NCCN), a common reaction product of HCN. The breakthrough time was defined as the time at which a concentration of 5 ppm HCN or NCCN was observed downstream from the sample.

Powder X-ray Diffraction:

Powder X-ray diffraction patterns were collected using a Phillips PW 1720 X-ray generator operated at a voltage of 40 kV and a current of 30 mA. The system is equipped with a Cu Kα radiation source (wavelength = 1.54178 Å) and a diffracted beam monochromator. Typical conditions were a scan rate of 0.05°/step and a dwell time of 40 s/step. The samples were ground into fine powder and mounted on an aluminum sample holder.

Surface Area and Pore Size Measurements:

N_2 adsorption isotherm and the pore size distribution were determined using a Micromeritics ASAP2010 at 77K. Samples were degassed at 100°C for 2-3 days before the

measurement to remove residual moisture. Pore size distributions were determined using the BJH method (1-300nm) using software supplied by Micromeritics (ASAP 2010 V5.03 C). The BJH method is a known method and is described at E.P. Barrett, L.G. Joyner, P.H. Halenda, J. Am. Chem. Soc. 73 (1951) 373.

Particle Size Measurements:

Particle size measurements (d(0.1), d(0.5) and d(0.9)) were made on a Mastersizer 2000 (Ver. 5.60) equipped with a Hydro2000S accessory from Malvern Instruments following 2 minutes of sonication using deionized water as a dispersant.

Table 1. Selected Characterization Data for Examples 1-5.

Example	Particle Size d(0.1,0.5,0.9) (μm)	Phase by XRD	BET Surface Area (m^2/g)	BJH Average Pore Volume (cm^3/g)	BJH Average Pore Size (nm)
1	7.4, 27.0, 58.1	2-line ferrihydrite	302.5	0.13	2.1
2	12.0, 29.2, 56.3	2-line ferrihydrite	289.0	0.17	2.2
3	11.8, 28.4, 53.5	2-line ferrihydrite	305.2	0.14	2.1
4	10.9, 31.2, 64.0	2-line ferrihydrite	329.9	0.14	1.9
5	11.0, 34.2, 75.5	2-line ferrihydrite	276.8	0.085	1.7

Table 2. Selected Characterization Data for Examples 6.

Example	Particle Size d(0.1,0.5,0.9) (μm)	Phase by XRD	BET Surface Area (m^2/g)	BJH Average Pore Volume (cm^3/g)	BJH Average Pore Size (nm)
6	8.7, 127.7, 615.9	2-line ferrihydrite	366.7	0.25	2.7

The samples of Examples 1-5 were challenged with vapors or gases using the test methods described above. The test results are shown below in Table 3 along with the test results from commercially available Calgon URC, a whetlerite multigas adsorbant prepared by impregnation of activated carbon with copper compounds, molybdenum compounds and salts of sulfuric acid.

Table 3. Breakthrough Test Results

	Breakthrough Time (minutes)[5]			
Example[1,2,3]	**SO_2 (±10%)**	**NH_3 (±10%)**	**HCN (±6%)**	**NCCN (±6%)**
Calgon URC[4]	44	52	111	105
1	97	110	6	21 (0.6 ppm)
2	156	69	35	53 (0.4 ppm)
3	165	113	106	100
4	165	173	165	153
5	67	275	15	12

[1]All filter media granules tested at 20x40 mesh size.
[2]Sample volume: 1 cc (SO_2, NH_3); 1.7 cc (HCN/NCCN)
[3]Average of 3 tests for breakthrough times
[4]Calgon URC (as received), commercially available from Calgon Carbon Company, Pittsburgh, PA, USA.
[5]For samples where NCCN was not observed to reach breakthrough concentration during HCN testing, NCCN breakthrough time is listed with the detected concentration of NCCN at the end of the test in parenthesis.

Table 4. Breakthrough Test Results

	Breakthrough Time (minutes)[5]			
Example[1,2,3]	**SO_2 (±10%)**	**NH_3 (±10%)**	**HCN (±6%)**	**NCCN (±6%)**
Calgon URC[4]	44	52	111	105
6	220	80	123	133

[1]All filter media granules tested at 20x40 mesh size.
[2]Sample volume: 1 cc (SO_2, NH_3); 1.7 cc (HCN/NCCN)
[3]Average of 3 tests for breakthrough times
[4]Calgon URC (as received), commercially available from Calgon Carbon Company, Pittsburgh, PA, USA.
[5]For samples where NCCN was not observed to reach breakthrough concentration during HCN testing, NCCN breakthrough time is listed with the detected concentration of NCCN at the end of the test in parenthesis.

Thus, embodiments of FILTER MEDIA FOR RESPIRATORY PROTECTION are disclosed.

All references and publications cited herein are expressly incorporated herein by reference in their entirety into this disclosure, except to the extent they may directly contradict this disclosure. Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that a variety of alternate and/or equivalent implementations can be substituted for the specific embodiments shown and described without departing from the scope of the present disclosure. This application is intended to cover any

adaptations or variations of the specific embodiments discussed herein. Therefore, it is intended that this disclosure be limited only by the claims and the equivalents thereof. The disclosed embodiments are presented for purposes of illustration and not limitation.

What is claimed is:

1. A composition comprising:

a doped ferrihydrite material having an average pore size (BJH method) in a range from 1 to 3 nm and a surface area (BET) of at least 200 m^2/g or at least 250 m^2/g or at least 300 m^2/g.

2. The composition according to claim 1, wherein the doped ferrihydrite material has a molar ratio of iron:dopant in a range from 95:5 to 75:25 or from 90:10 to 80:20.

3. The composition according to claim 1 or 2, wherein the doped ferrihydrite material includes dopant material comprising a metal such as Cu, Zn, Ca, Ti, Mg, Zr, Mn, Al, Si, Mo, Ag or mixtures thereof.

4. The composition according to claim 1 or 2, wherein the doped ferrihydrite material includes dopant material being Cu or Zn.

5. The composition according to any of the preceding claims, wherein the doped ferrihydrite material are granules having a mesh size in a range from 12 to 50 or from 20 to 40 U.S. standard sieve series.

6. The composition according to any of the preceding claims, wherein the doped ferrihydrite material are in a form of compression derived granules.

7. The composition according to any of claims 1 to 4, wherein the doped ferrihydrite material defines aggregate particles having a median largest lateral dimension in a range from 1 to 100 micrometers or from 15 to 45 micrometers or from 20 to 40 micrometers or about 30 micrometers.

8. The composition according to any of the preceding claims, wherein the doped ferrihydrite material has a moisture content of less than 10% by wt or less than 5% by wt.

9. A respiratory protection filter comprising:

a housing having an air stream inlet and an air stream outlet and containing an amount of filtration media in fluid connection and between the air stream inlet and the air stream outlet, the filtration media comprising:

free-standing granular doped ferrihydrite material.

10. The respiratory protection filter according to claim 9, wherein the doped ferrihydrite material is capable of removing a hazardous gas from an air stream passing through the filtration media at ambient conditions or atmospheric pressure and -20 to 40 degrees centigrade and 5% to 95% relative humidity.

11. The respiratory protection filter according to any of claims 9 or 10, wherein the filtration media comprises at least 20% by wt or at least 30% by wt or at least 50% by wt doped ferrihydrite material.

12. The respiratory protection filter according to any of claims 9 to 11, wherein the doped ferrihydrite material has a molar ratio of iron:dopant in a range from 95:5 to 75:25 or from 90:10 to 80:20

13. The respiratory protection filter according to any of claims 9 to 12, wherein the doped ferrihydrite material includes dopant material comprising a metal such as Cu, Zn, Ca, Ti, Zr, Mg, Mn, Al, Si, Mo, Ag or mixtures thereof.

14. The respiratory protection filter according to any of claims 8 to 13, wherein the doped ferrihydrite material includes dopant material being Cu or Zn.

15. The respiratory protection filter according to any of claims 8 to 14, wherein the doped ferrihydrite material defines granules having a mesh size in a range from 12 to 50 or from 20 to 40 U.S. standard sieve series.

16. A method, comprising:

combining a hydrated iron (III) salt with a metal dopant salt to form a mixture;

blending a bicarbonate material with the mixture to form a wet doped ferrihydrite material and salt co-product;

drying the wet doped ferrihydrite material and salt co-product to a moisture content of less than 10% by wt or less than 5% by wt to form a dried doped ferrihydrite material and salt co-product;

washing away the salt co-product with water to form a wet doped ferrihydrite material; and

drying the wet doped ferrihydrite material to a moisture content of less than 10% by wt or less than 5% by wt to form a dried doped ferrihydrite material.

17. The method according to claim 16, wherein the bicarbonate material is sodium bicarbonate.

18. The method according to claims 16 or 17, wherein the method has a processing temperature for all method steps that is no greater than 115 degrees centigrade.

19. The method according to claims 16 to 18, wherein the drying steps removes only water or moisture from the wet doped ferrihydrite material and salt co-product or the wet doped ferrihydrite material.

20. The method according to claims 16 to 19, wherein the metal dopant salt comprises Cu or Zn.

21. The method according to claims 16 to 20, wherein the combining step comprises combining a molar ratio of hydrated iron (III) salt:metal dopant salt in a range from 95:5 to 75:25 or from 90:10 to 80:20.

22. The method according to claims 16 to 21, wherein the mixture is a powder mixture and the bicarbonate material is a powder bicarbonate material.

23. The method according to claims 16 to 22, further comprising the step of granulating or compressing the doped ferrihydrite material into granules having a mesh size in a range from 12 to 50 or from 20 to 40 U.S. standard sieve series.

24. The method according to claims 16 to 23, further comprising placing the doped ferrihydrite material into a respiratory protection filter.

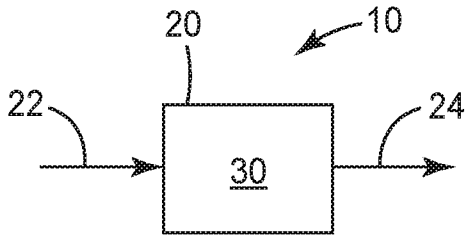

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22
24
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FIG. 1

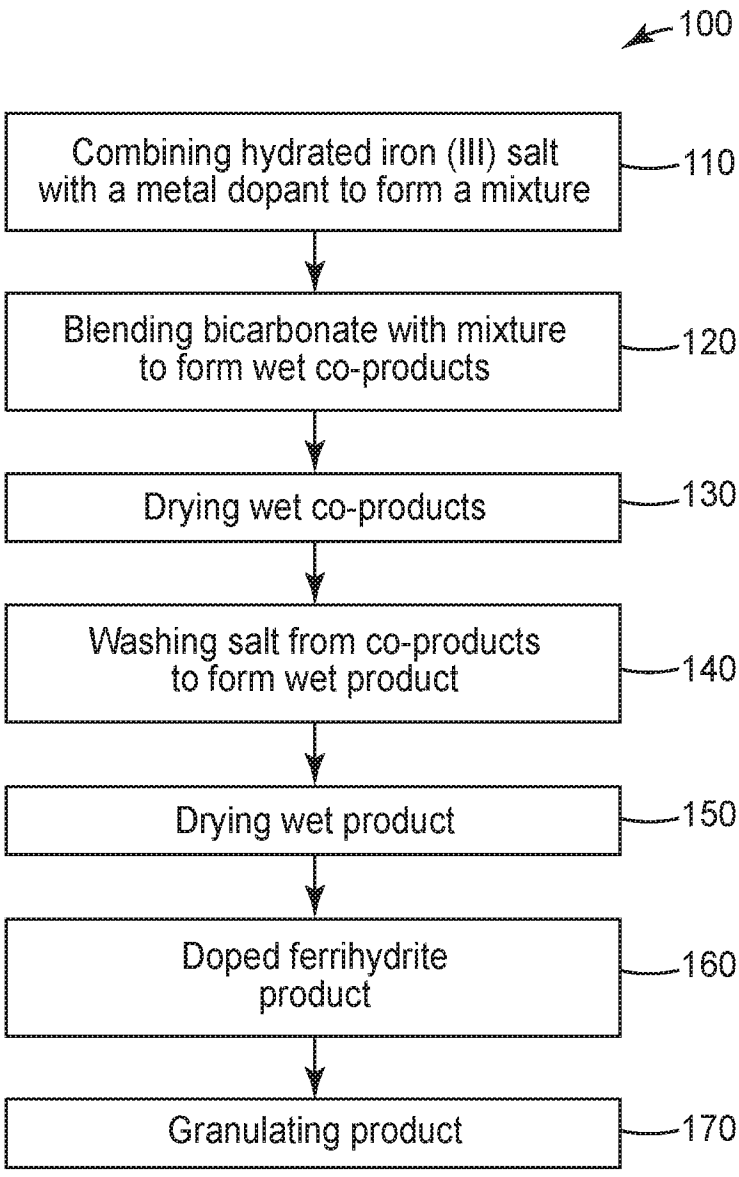

100
Combining hydrated iron (III) salt with a metal dopant to form a mixture
110
Blending bicarbonate with mixture to form wet co-products
120
Drying wet co-products
130
Washing salt from co-products to form wet product
140
Drying wet product
150
Doped ferrihydrite product
160
Granulating product
170

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/028364

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/06 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

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, COMPENDEX, EMBASE, 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 2011/201702 A1 (BALI SUMIT [US] ET AL) 18 August 2011 (2011-08-18) paragraph [0037] paragraph [0040] - paragraph [0041] paragraph [0043] - paragraph [0045] paragraph [0056] - paragraph [0059] -----	1-8
X	US 5 580 839 A (HUFFMAN GERALD P [US] ET AL) 3 December 1996 (1996-12-03) column 2, line 41 - column 3, line 5 examples 1,2,8,9 ----- -/--	1-3

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 July 2016	13/07/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zalfen, Alina

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/028364

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/247636 A1 (SCHLEGEL ANDREAS [DE]) 10 November 2005 (2005-11-10) paragraph [0005] - paragraph [0006] paragraph [0023] paragraph [0037] paragraph [0039] - paragraph [0040] paragraph [0042] paragraph [0054] - paragraph [0055] paragraph [0058] - paragraph [0062] paragraph [0065] - paragraph [0066] examples 1,5	1-24
A	US 2013/302231 A1 (AIKENS CHRISTOPHER L [US] ET AL) 14 November 2013 (2013-11-14) paragraph [0007] - paragraph [0008]	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2016/028364

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011201702 A1	18-08-2011	NONE	
US 5580839 A	03-12-1996	NONE	
US 2005247636 A1	10-11-2005	AT 399147 T	15-07-2008
		CN 1689694 A	02-11-2005
		DE 102004016601 A1	13-10-2005
		EP 1582505 A1	05-10-2005
		ES 2308326 T3	01-12-2008
		JP 5150041 B2	20-02-2013
		JP 2005288439 A	20-10-2005
		JP 2012071305 A	12-04-2012
		US 2005247636 A1	10-11-2005
US 2013302231 A1	14-11-2013	CA 2824586 A1	26-07-2012
		US 2013302231 A1	14-11-2013
		WO 2012100113 A1	26-07-2012