# A METHOD OF PRODUCING A MATERIAL FOR ADSORPTION OF FLUIDS

## Technical Field

The present invention generally relates to an adsorption material for adsorbing fluid. The present invention also relates to an apparatus comprising the adsorption material and to a vehicle for transporting fluids.

## Background

Ammonia is widely used as a raw material for chemical processes. Ammonia is a corrosive and very reactive gas that is toxic to humans in sufficient quantities. Therefore, in many industrial processes, it is important to remove ammonia from the process or exhaust stream.

Ammonia is commonly stored as a liquefied gas under high pressure. This requires the use of pressure vessels, which is expensive. It is also potentially dangerous to store ammonia at high pressures because if the pressure vessels fails (i.e. due to cracks formed in the surface of the vessel), a sudden release of ammonia to the atmosphere may result. A sudden release of ammonia gas may be explosive. Furthermore, the release of a large quantity of ammonia gas to the atmosphere could be toxic to humans and other animals.

It will be appreciated that the high pressure storage of ammonia is a particular problem when the ammonia gas needs to be transported from one locale to another.

An alternative to storing ammonia at high pressures is to store ammonia on an adsorbent material. However, the capacity of known absorbent material has been quite

low, particularly at ambient temperatures and pressure. To overcome this problem, it is known to adsorb and desorb gas using extreme conditions (such as relatively high pressures and low temperatures) to increase the storage capacity of ammonia on the adsorbent material.

There is a need to provide adsorbent materials that overcome or at least ameliorate one or more of the disadvantages described above.

There is a need to provide adsorbent materials that can adsorb gases reversibly under relatively moderate temperatures and pressures and yet posses relatively high adsorption capacity.

There is also a need to provide adsorbent materials that can adsorb solutions such as aqueous ammonia solution.

## Summary

According to a first aspect, there is provided a method of producing an adsorbent material capable of adsorbing fluid, the method comprising the step of exposing an activated carbon material to a polar organic solvent before impregnating the activated carbon material with a salt.

According to a second aspect, there is provided a method of producing an adsorbent material capable of adsorbing fluid, the method comprising the steps of:

(a) exposing an activated carbon material to a polar organic solvent;

(b) removing at least a portion of the polar organic solvent from the activated carbon material;

(c) introducing a salt to the activated carbon material in the presence of an aqueous solution; and

(d) removing the aqueous solution from the activated carbon material.

The method may further comprise the step of calcinating the adsorbent material.

According to a third aspect, there is provided an adsorbent material made in a method according to the first aspect or the second aspect.

According to a fourth aspect, there is provided the use of an adsorbent material made in a method according to the first aspect or the second aspect, for adsorption of a fluid.

According to a fifth aspect, there is provided an apparatus for storing fluid comprising:

a housing having a chamber for enclosing adsorbent material therein, the adsorbent material comprising an activated carbon impregnated with a salt; and

at least one conduit extending through the housing and into the chamber for transfer of fluid to and from the chamber.

In one embodiment of the fifth aspect, the adsorbent material is made in a method according to the first aspect or the second aspect.

According to a sixth aspect, there is provided an apparatus for storing fluid comprising:

a housing having a chamber for locating a fluid adsorbent material therein;

at least one conduit extending through the housing and into the chamber for transfer of fluid to and from the chamber; and

a heat exchanger for driving adsorption of fluid onto the fluid adsorbent material or for driving desorption of fluid from the fluid adsorbent material, or both.

According to a seventh aspect, there is provided a vehicle for transporting fluids, the vehicle comprising:

a housing having a chamber for locating a fluid adsorbent material therein; and

at least one conduit extending through the housing and into the chamber for transfer of fluid to the chamber or from the chamber, or both.

In one embodiment of the seventh aspect, the vehicle is a self-propelled vehicle.

In one embodiment of the seventh aspect, the fluid adsorbent material is made in a method according to the first aspect or the second aspect.

**Definitions**

The following words and terms used herein shall have the meaning indicated:

The term 'fluid' is to be interpreted broadly to refer to both a gas phase fluid and a liquid phase fluid.

The term 'activated carbon' is to be interpreted broadly to include any carbon material that is capable of adsorption of fluid.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood

that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range.

## Detailed Disclosure of Embodiments

*Process for producing an adsorbent material*

An embodiment disclosed herein relates to a method of making an adsorbent material. The method may provide improved impregnation of salt, and in particular $CaCl_2$, within the adsorbent material. Due to the gas adsorption capacity of the produced adsorbent material, the method may realise benefits in scalability of the process to large-scale applications.

The activated carbon material may be selected from the group consisting of carbon granules, carbon fibers, carbon nano-fiber, graphite material, carbon matrix, carbon powder and carbon felt.

The salt may be a metal halide salt. The metal may be selected from the group consisting of group IA metals, group IIA metals and group VIII metals of the Periodic Table of elements, and mixtures thereof. The halide may be selected from the group consisting of fluoride, bromide, chloride, iodide and mixtures thereof.

In one embodiment, the metal is calcium. In another embodiment the halide is chloride. In yet another embodiment, the salt is calcium chloride ($CaCl_2$). Other exemplary salts may be barium chloride, nickel chloride, magnesium chloride, cobalt chloride and strontium chloride, bromide fluoride and calcium iodide.

The salt may be a solid or a salt solution. The weight % of salt relative to carbon in the material may be selected from the range of groups consisting of about 10% to about 50%; about 20% to about 50%; about 30% to about 50%; about 40% to about 50%; 10% to about 40%; about 10% to about 30%; about 10% to about 20%. Exemplary weight ratios of salt:carbon in the material may be selected from the group 10:90, 20:80, 25:75, 30:70 and 35:65. The desired salt:carbon ratio may be obtained by adjusting the amount of salt introduced to a given weight of carbon material.

It has surprisingly been found by the inventor that the introduction of salt to carbon in the presence of a polar organic solvent will lead to enhanced adsorption abilities of the carbon material. Without being bound by theory, it is thought that the polar organic solvent may assists the salt in impregnating the activated carbon material.

The polar organic solvent may be a low carbon polar organic solvent. The polar organic solvent may have from 1 to 6 carbon atoms, 2 to 6 carbon atoms, 2 to 4 carbon atoms or from 1 to 4 carbon atoms. In one embodiment, the low carbon polar organic solvent is selected from the group consisting of alcohols, ethers, aldehydes, ketones and carboxylic acids.

In one embodiment, the alcohols are selected from the group consisting of methanol, ethanol, propanol, butanol and hexanol.

In one embodiment, the ethers are selected from the group consisting of dimethyl ether, ethyl methyl ether, diethyl ether, ethyl propyl ether and dipropyl ether.

In one embodiment, the aldehydes are selected from the group consisting of formaldehyde, acetaldehyde, propanaldehyde, butyraldehyde, iso-butyraldehyde.

In one embodiment, the ketones are selected from the group consisting of acetone, propanone, butanone and iso-butanone.

The activated carbon material may be exposed to the polar organic solvent at a temperature selected from the group consisting of about 20°C, about 25°C, about 30°C, about 35°C, about 40°C and about 45°C. In one embodiment the activated carbon material is exposed to the polar organic solvent at an ambient temperature range of about 18 to about 30°C.

The activated carbon material may be exposed to the polar organic solvent at a pressure selected from the group consisting of about 0.5 bar to about 4 bar, 0.8 bar to about 3, about 0.9 bar to about 2, and about 0.9 bar to about 1.1. In one embodiment the activated carbon material is exposed to the polar organic solvent at a pressure of about 1 bar.

In one embodiment, the activated carbon material is exposed to the polar organic solvent at a temperature selected from the group consisting of about 10°C to about 80°C, about 15°C to about 50°C, about 15°C to about 40°C, about 15°C to about 30°C, about 20°C to about 30°C. In one embodiment, the activated carbon material is exposed to the polar organic solvent at ambient temperature and pressure. It is a particular advantage of the embodiments, that the impregnation of the salt into the activated carbon material may be undertaken at low temperatures and pressures as this may reduce the costs associated with production of the adsorbent material.

The polar organic solvent may be removed from the activated carbon material by one or more of heating, desiccation, evaporation, calcination, drying, drying under vacuum, or drying using heated gas.

In one embodiment, the polar organic solvent is removed by evaporating the solvent and further passing a heated gas, such as nitrogen, through the material. The evaporation may be carried out at a temperature range selected from a group consisting of 50°C to 100°C, 60°C to 100°C, 60°C to 90°C, 60°C to 80°C, 60°C to 70°C. In one embodiment, the evaporation is carried out at a temperature in the range 60 to 100°C. The heated gas used for drying the activated carbon material may be any gas that is inert to the polar organic solvent. In one embodiment the gas is nitrogen.

The aqueous solution may be removed from the activated carbon material by one or more of heating, desiccation, evaporation, calcination, drying, drying under vacuum, or drying using heated gas. In one embodiment the aqueous solution is removed by evaporation followed by passing a heated gas through the activated carbon material. The heated gas may be any gas that is inert to the activated carbon material. In one embodiment the heated gas is nitrogen.

The method may further involve calcination of the activated carbon material. Calcination may be carried out at a temperature selected from a group consisting of about 100°C to about 500°C, about 150°C to about 450°C, about 200°C to about 400°C, about 300°C to about 400°C, about 120°C to about 300°C, about 150°C to about 250°C, and about 150°C to about 200°C.

In one embodiment, calcination is carried out at about 300°C. In another embodiment, calcination is carried out at about 175°C, particularly where a hydrous salt is used such as $CaCl_2 \cdot H_2O$. The fluid adsorption material prepared according to the disclosed method may be capable of adsorbing a fluid containing atoms selected from the group consisting of nitrogen (N), oxygen (O), sulfur (S),

hydrogen (H), chlorine (Cl), fluorine (F), carbon (C), and combinations thereof. In one embodiment, the fluid may be a gas selected from the group consisting of ammonia, hydrogen sulfide, sulfur oxides such as $SO_x$, hydrogen chloride, chlorine, nitrogen oxide such as NOx, formaldehyde, polar hydrocarbon and mixtures thereof. In another embodiment, the fluid is liquid ammonia.

*Vehicle for Fluid Transport*

A disclosed embodiment also relates to a vehicle for transporting fluids. The vehicle comprises a housing having a chamber for locating a fluid adsorbent material therein. A conduit extends through the housing and into the chamber for transfer of fluid to and from the chamber. The fluid adsorbent material provided in the housing may be any absorbent capable of adsorbing fluid such as ammonia gas or ammonia liquid. The vehicle may be a self-propelled vehicle such as a truck or a tractor. In other embodiments, the vehicle may be a trolley or a trailer that is propelled by another vehicle.

The vehicle may comprise a heat exchanger for driving adsorption of fluid onto the fluid adsorbent material or for driving desorption of fluid from the fluid adsorbent material, or both. The heat exchanger may be located within the housing.

The vehicle may comprise a fluid pump for moving fluid to and from the chamber. The fluid pump may comprise a blower for moving gas to and from the chamber.

The vehicle may comprise a plurality of housings, wherein the chambers of said plurality of housings are capable of being in fluid communication with each other.

*Fluid Storage Apparatus*

In another embodiment, there is also disclosed a fluid storage apparatus comprising a housing having a chamber for locating a fluid adsorbent material therein. The housing also has at least one conduit extending through the housing and into the chamber for transfer of fluid to and from the chamber; and a heat exchanger for driving adsorption of fluid onto the fluid adsorbent material or for driving desorption of fluid from the fluid adsorbent material, or both. The heat exchanger may be a conduit extending into the housing so that the outer surface of the conduit may be in contact with the fluid adsorbent material in use. The conduit may be in the form of a disc and may be provided at the bottom of the housing. In use, cooled fluid may be provided to the heat exchanger to drive the adsorption of fluid onto the fluid adsorbent material. Heated fluid may also be provided to the heat exchanger to drive the desorption of fluid from the fluid adsorbent material.

## Brief Description Of Drawings

The accompanying drawings illustrate disclosed embodiments and serve to explain the principles of the disclosed embodiments. It is to be understood, however, that the drawings are designed for the purpose of illustration only, and not as a definition of the limits of the invention.

**Fig. 1** is a process flow diagram of a process for preparing an adsorbent material according to a disclosed embodiment.

**Fig. 2** is a cross-sectional view of a mesh cylinder used to contain adsorbent material therein.

**Fig. 3** is a cross-sectional view of an adsorption cylinder containing the mesh cylinder.

**Fig. 3a** is a top view of a cooling disk located in the adsorption cylinder of Fig. 3.

**Fig. 3b** is a side view of the cooling disk of Fig. 3a.

**Fig. 4** is a schematic diagram of a metal container comprising a plurality of the adsorption cylinders of Fig. 3.

**Fig. 4a** is a cross-sectional front view of an assembly comprising a plurality of metal containers as depicted in Fig 4.

**Fig. 4b** is top view of the assembly of Fig 4a.

**Fig. 5** is a schematic diagram of a vehicle for transporting gas comprising a plurality of the metal containers of Fig 4.

**Fig. 6** is a schematic diagram of an experimental system that was used to determine dynamic adsorption measurement data.

**Fig. 7a(I)** is a SEM photograph of a sample of an adsorption material comprising 45 wt % of $CaCl_2$ at a magnification of 1000.

**Fig. 7a(II)** is a SEM photograph of a sample of an adsorption material comprising 45 wt % of $CaCl_2$ at a magnification of 10000.

**Fig. 7b(I)** is a SEM photograph of a sample of an adsorption material comprising 35 wt % of $CaCl_2$ at a magnification of 1000.

**Fig. 7b(II)** is a SEM photograph of a sample of an adsorption material comprising 35 wt % of $CaCl_2$ at a magnification of 10000.

**Fig 7c** is a SEM photograph of a sample of an adsorption material prepared according to a disclosed embodiment comprising 35 wt% of $CaCl_2$.

**Fig 7d** is a SEM photograph of a sample of an adsorption material comprising 35 wt% of $CaCl_2$ not prepared according to disclosed embodiment.

**Fig. 8** is a graph showing temperature and weight data at changing partial pressures of ammonia over time in the adsorber of Fig. 6 .

**Fig. 9** is a graph showing adsorption capacity (kg ammonia gas per kg absorbent) as a function of partial pressure of ammonia gas and gas flow velocity.

**Fig. 10** is a graph showing the pressure drop as a function of gas flow velocity in an adsorption cell.

**Fig 11** shows a process flow diagram of a testing facility utilising the metal containers depicted in Fig4.

**Fig 12** is a graph showing an adsorption temperature profile of an adsorption cylinder of the test facility in Fig 11.

**Fig. 13** is a graph showing a release rate of ammonia vapor from the adsorption cylinder of the test facility in Fig 11.

**Detailed description**

*Process & Equipment for making ACF adsorbent material*

Fig. 1 shows a schematic diagram of a process 24 for producing adsorbent material capable of adsorbing fluids such as ammonia gases and liquids. The process 24 in the disclosed embodiment utilizes Activated Carbon Felt (ACF) for adsorption and desorption of ammonia gas.

The process 24 comprises an Activated Carbon Felt (ACF) module 1 comprising a tank 2 of methanol and a mesh cylinder 13 containing activated carbon felt (ACF) therein. A more detailed view of the mesh cylinder 13 can be seen in Fig. 2.

The mesh cylinder 13 comprises a circular shaped stainless steel mesh side 15, a stainless steel plate top 17 and a stainless steel plate bottom 19 surrounding an enclosure 21. The enclosure 21 is packed with activated carbon material in the form of activated carbon felt (ACF). The ACF may be obtained commercially such as from Khimvolokno, of Minsk, Belarus under the trade name BUSOFIT T-055 or Tonghui Industrial & Trading Co. Ltd of Jiangsu, China.

The mesh cylinder also has a conduit 22 extending from an aperture (not shown) provided in the top plate 17 to the bottom plate 19. The conduit 22 is also made of stainless steel mesh to allow the flow of gas to and from the ACF.

The pore size of the mesh side 15 and conduit 22 is sufficient to allow fluids to flow into and out of the

mesh cylinder but is small enough to prevent the ACF from escaping from the mesh cylinder 13.

Fig. 3 shows a detailed cross-sectional view of a housing in the form of an adsorption cylinder 12. The adsorption cylinder 12 comprises a metal cylinder 14 surrounding an enclosure 16. The metal cylinder 14 is connected to a top metal plate 18 and a bottom metal plate 20. The conduit 22 extends through an aperture provided in the top metal plate 18 and into the enclosure 16. The conduit 22 is sealed at the end extending into the enclosure by a bottom plate 19. Another conduit 23 extends through an aperture provided in the bottom metal plate 20 and into the enclosure 16. The enclosure 16 has a mesh cylinder 13 located therein which rests on support 17.

The cylinder 12 includes a heat exchanger in the form of a cooling water disk 101 between the mesh cylinder 13 and the support 17. Figs. 3a,3b respectively show a top and side view of the cooling disk 101. The disk has a tube provided therein in which water flows during use to facilitate heat transfer. The channel spirals along the body of the disk and water is injected in a circumferential way from a number of holes in the tube, to promote turbulent flow of the water and thereby to promote heat transfer in use.

In use, the cooling water disk 101 is in fluid communication with a cooling fluid source when the adsorption cylinder 12 is in an adsorption mode. Cooling water flowing through the cooling disk 101 removes heat of adsorption and drives adsorption occurring onto the ACF material provided in the mesh cylinder 13. In a desorption mode, cooling water may not flow through the cooling water disk 101. In other embodiments, hot water may flow into the cooling water disk 101 to further drive

the desorption of gas from the ACF material provided in the mesh cylinder 13.

In embodiments where the cylinder 14 is provided in a gas transportation system such that the cylinder resides on a truck platform, hot water from the truck engine may be used as a heat water source.

Referring again to Fig. 3, the conduit 23 is connected to a gas pipe (not shown) via the aperture in the bottom metal plate 20. The gas pipe supplies gas to the conduit 23 when the adsorption cylinder 12 is operated in an adsorption mode. Another gas pipe (not shown) is connected to the conduit 22 which provides a vent for the gas when the adsorption cylinder 12 is operated in a desorption mode. This pipe also provides a vent for lean gas when the adsorption cylinder 12 is operated in an adsorption mode. In other embodiments, the aperture extending through the top plate 18 and/or the aperture extending through the bottom plate 20 may be provided with a gas valve to control the flow of gas to and from the conduit 22.

In use, gas that is to be adsorbed is provided to the adsorption cylinder 12 via a pipe (not shown) connected to the conduit 23. The gas enters the mesh cylinder 13 through the outer cylindrical mesh surface 16a and is adsorbed onto the ACF adsorbent material located in the mesh cylinder enclosure 21. The lean gas then flows through the inner cylindrical mesh surface 16b and enters the conduit 22.

When the adsorption cylinder 12 is operated in a desorption mode, the gas adsorbed on the adsorbent material flows through inner cylindrical mesh surface 16b and exits via conduit 22.

The metal cylinder 14 is made of a material that is resistant to corrosion in the gaseous environments to

which it is exposed. In this embodiment, the metal is stainless steel as it does not react with ammonia gas.

It will be appreciated that in this embodiment, the mesh cylinders 13 are used in the adsorption cylinder 12 because it is convenient to contain the ACF in the mesh cylinder 13 when the ACF material is subjected to the process 24 as will be described further below. However it should be realised that the mesh cylinders 13 are optional and the ACF may be packed within the chamber adsorption cylinder 12. Furthermore, in other embodiments, the conduit may be the form of a simple pipe that extends through one of the top plate 18, cylinder side 14 or bottom 20. Furthermore, in other embodiments, the conduit 22 may extend all the way through the interior of the adsorption cylinder 12.

The adsorption cylinder 12 may be used to store and release gasses such as ammonia. It will be appreciated that the adsorption cylinder 12 can be transported on a vehicle so that the adsorption cylinder 12 is a convenient receptacle to store and transport gas.

It will also be appreciated, that in other embodiments, the housing may be capable of storing multiple mesh cylinders 13 therein. Figure 4 shows a housing in the form of metal container 30 having a plurality of mesh cylinders (13a,13b,13c,13d,13e) comprising the activated carbon felt located therein. The metal container 36 is provided with an inlet conduit 38 for flow of gas into the metal container 36 and thereby the mesh cylinders (13a,13b,13c,13d,13e). The metal container 36 is also provided with an outlet conduit 40 for flow of gas from the mesh cylinders (13a,13b,13c,13d,13e).

A dual train of metal containers as described above will now be described with reference to Fig 4a and Fig

4b, which respectively show a cross-sectional front view and a top view of an assembly 121 comprising plurality of metal containers (30a,30b,30c,30d,30e,30a',30b', 30c',30d',30e') of Figure 4. The metal containers (30a, 30b,30c,30d,30e,30a',30b',30c',30d',30e') are arranged as shown in Fig 4a and Fig 4b to form two metal container trains 136 and 136'. Each of the metal containers (30a, 30b,30c,30d,30e,30a',30b',30c',30d',30e') contain multiple adsorption cylinders 13 as described.

The train 136 comprises metal containers (30a,30b,30c,30d,30e) while the train 136' comprises metal containers (30a',30b',30c',30d' 30e'). The structures of the two trains (136,136') are identical. The structure of train 136 is described below.

The metal containers (30a,30b,30c,30d,30e) of the train 136 are enclosed in a housing 132. The train 136 is provided with an inlet conduit 122 for flow of gas into the metal containers (30a,30b,30c,30d,30e) and an outlet conduit 124 for flow of gas out of the metal containers (30a,30b,30c,30d,30e). Butterfly valves (126,128) are respectively provided on the inlet conduit 122 and the outlet conduit 124 for regulating gas flow into and out of the assembly 121.

The inlet conduit 122 extends into the housing 132 via perforated conduit 130 that is in fluid communication with the internal metal containers (30a,30b,30c,30d,30e).

An outlet conduit 134 is also provided on the top of the assembly 121, and have a butterfly valve 128. The outlet conduits (40a, 40b, 40c, 40d, 40e) of the metal containers (30a, 30b, 30c, 30d, 30e) are in fluid communication with the perforated conduit 134.

In use, the conduit 130 provides gas to the metal containers (30a, 30b, 30c, 30d, 30e). The gas is adsorbed on the ACF adsorbent material located in the adsorption

cylinders located within the metal containers (30a, 30b, 30c, 30d, 30e). Outlet gas then passes from outlet conduits (40a, 40b, 40c, 40d, 40e) and connect to the common outlet conduit 134 so that the outlet gas can exit out of the (30a, 30b, 30c, 30d, 30e).

*Process Equipment*

Process equipment used in the impregnation process of a disclosed embodiment will now be described. Fig. 1 shows a process flow diagram of a process for preparing an adsorbent material according to a disclosed embodiment. The process involves three tanks namely, a methanol tank 2, a water tank 3 and a $CaCl_2$ (aq) tank 4. All of the tanks (2,3,4) have a diameter sufficiently large such that the mesh cylinder 13 is able to be located in the tanks (2,3,4) during impregnation of the $CaCl_2$. The $CaCl_2$ (aq) tank 4 is connected to a vacuum pump 9 via a cold trap (5).

The $CaCl_2$ (aq) tank 4 is also connected to a nitrogen source to allow heated nitrogen gas to flow into the tank. The nitrogen is initially stored as liquid nitrogen in tank 11, which is evaporated in an vaporizer 10 and further heated with an electric heater 9. The nitrogen gas reports to the base of the tank (4) and is then passed through the tank (4) via a valve.

*Example 1 - Adsorbent Material*

An example will now be described in which $CaCl_2$ salt is impregnated into ACF using the process equipment described above with reference to Fig. 1.

The process involved introducing and removing a mesh cylinder 13 comprising activated ACF into and out of the methanol tank 2. This was repeated 10 times to ensure that the ACF was completely drenched with methanol.

The mesh cylinder 13 was removed from the methanol tank and immersed in the distilled water tank. The mesh cylinder 13 was introduced into and removed from the distilled water tank. This was repeated 10 times to rinse methanol from the ACF.

The mesh cylinder 13 was removed from the distilled water tank 3 and immersed in the $CaCl_2$ (aq) tank 4 for 24 hours. The concentration of $CaCl_2$ (aq) was adjusted to provide a $CaCl_2$:Carbon ratio of 35:65 by weight.

After soaking, the salt solution was drained and further evacuated by pumping. A cold trap (5) was used to prevent water from entering into the rotary oil pump. Heated nitrogen gas at a temperature of 150°C was then passed through the mesh cylinder 13 to remove any remaining traces of methanol.

The mesh cylinder 13 was then placed inside a furnace for 12 hours to further evaporate any remaining solvent. The temperature of the furnace was in the range of $60^0$C-$100^0$C. Once the solvent was evaporated, the mesh cylinder 13 was further calcined in a furnace at $300^0$C for 1 hour.

In this process, the affinity of methanol to $CaCl_2$ enables a thorough penetration of $CaCl_2$ into the ACF adsorbent material, thereby providing an improved impregnation. Without being bound by theory, it is thought that the overall reaction may be represented as follows:

$$CaCl_{2\,(s)} + 2CH_3OH_{(l)} \leftrightarrow CaCl_2 \cdot 2CH_3OH_{(l)}$$

*Comparative Example*

Another adsorbent material was prepared by impregnating $CaCl_2$ salt into ACF using the process

equipment described above with reference to Fig 1. The process was substantially similar to the one described in Example-1 with the exception that the ACF material was not treated with methanol.

*SEM Observations*

SEM (Scanning Electron Microscope) studies were undertaken from two samples of the adsorbent material in which the weight ratio of $CaCl_2$:ACF was 35wt% and 45wt% respectively. Figure 7a and 7b respectively show SEM photographs of the 35wt % and 45wt% $CaCl_2$:ACF samples. Fig. 7a(I) shows the 35wt % sample at a magnification of 1000 and Fig. 7a(II) shows the 35wt % sample at a magnification of 10000. Fig. 7b(I) shows the 45wt % sample at a magnification of 1000 and Fig. 7b(II) shows the 45wt % sample at a magnification of 10000. It can be seen from the magnified images that the calcium chloride was uniformly deposited on the active carbon fiber surface and throughout the body of the fiber.

SEM photographs were also taken for the samples prepared in Example 1 and in the comparative example. Figure 14a and 14b respectively show SEM photographs of samples of adsorbent material prepared by Example 1 and by in the comparative example. It can be seen from the images that the adsorbent material of Example 1 shows enhanced impregnation of $CaCl_2$ as compared to the adsorbent material of Comparative Example. Accordingly, this enhanced impregnation of $CaCl_2$ salt into the ACF fiber has resulted in a higher adsorption capacity ACF material that is capable of adsorption of gasses such as ammonia.

*Experimental System – dynamic adsorption data*

Figure 6 shows an experimental adsorption system 111 for measurement of dynamic adsorption data of the activated carbon material prepared in the above example. Through this experiment, adsorption data of the ACF adsorption material was obtained.

The experimental adsorption system 111 comprised a vessel 112 having a chamber therein. A gas inlet conduit 113 extends into the chamber and connects to two adsorption cylinders (not shown), which are the same design as the adsorption cylinder 12 described above, expect that the two adsorption cylinders are respectively 150mm long and 300mm long. ACF adsorption material prepared in the method described in Example 1 above was provided in each of the two adsorption cylinders. The two adsorption cylinders located in the vessel 112 were connected to a gas outlet 114.

The experimental adsorption system 111 also comprised a load cell 106 for measuring changes in weight of the vessel (and therefore adsorption/desorption of gas to and from the adsorption cylinders).

The experimental adsorption system 111 also comprised a Resistance Temperature Dependent (RTD) thermometer (102) in the center of the vessel 112 for recording the temperature of the adsorbent. An inflow velocity sensor 108 was also provided on the inlet conduit 113 for measuring gas flow velocity into the vessel 112 and outlet velocity sensor 110 was also provided on the outlet conduit 114 for measuring gas flow velocity from the vessel 112.

Butterfly valves (115,116) were respectively provided on the inlet conduit 113 and outlet conduit 114 for regulating gas flow.

The partial pressure of ammonia gas in the air was changed by varying the flow rate of ammonia gas. However, the maximum partial pressure in the experiment was maintained at less than the upper explosive limit of 25 volume % in air for safety reasons.

The volumetric flow rate was changed by an inverter frequency provided on a blower (not shown) and was calculated by measuring a flow velocity with the help of the inflow and outflow velocity sensors (108 and 110). The pressure drop was measured by two differential pressure gauges 117 that extend from the top of the vessel 112.

*Adsorption Capacity (Q)*

Figure 8 is a graph showing temperature and weight changes in adsorption material provided in the cylinders located in the vessel 112, corresponding to a change in ammonia gas flow rate through inlet conduit 113.

Fig. 9 is a graph showing adsorption capacity (kg ammonia gas per kg absorbent) as a function of partial pressure of ammonia gas and gas flow velocity.

It can be seen from Fig. 9 that adsorption capacity increases at higher flow velocity and at increasing partial pressure of ammonia gas.

It has advantageously been found that when the ACF adsorbent material was able to adsorb 0.4 kg ammonia/kg ACF adsorbent material at a temperature of 25°C and a pressure of about 1 bar (101.3 kPa). Conversely, when a sample of ACF adsorption material was not subjected to $CaCl_2$ impregnation, the ACF adsorption material adsorbed 0.09 kg ammonia/kg ACF felt under a temperature of 25°C and a pressure of about 1 bar (101.3 kPa).

Accordingly, using the $CaCl_2$ impregnation method disclosed above, it was possible to significantly enhance the adsorption capacity of the ACF material.

Figure 10 shows pressure drop dependent on flow velocity in the adsorption cylinder. In the system 111, it was found that when a contacting time of more than 2 seconds and a flow velocity of less than 0.15m/s was required, the minimum length of the adsorption cylinder was about 300 mm, and the minimum pressure head of a blower providing gas through the inlet 113 was about 500mm of water.

*Adsorption Heat (H)*

The measurements for determining the adsorption isotherm were taken by using a thermogravimetical apparatus (TG balance), in which the balance for weight measurement and sample space were separated by a magnetic suspension coupling so as to allow the measurements under the corrosive ammonia gas atmosphere. The adsorption heat was evaluated as 1078 kJ/kg-ammonia.

*Mass Transfer Coefficient $K_Fa_V$*

A mass transfer coefficient was obtained from the adsorption rate measurement data. Adsorption rate is given by the following equation.

$$\delta q_m / \delta t = k_F a_V (q-q_m)$$

where q is the equilibrium concentration of the gas and $q_m$ is the amount of gas adsorbed on the adsorption material.

From the obtained experimental values of $\delta q_m / \delta t$ and $(q-q_m)$, the mass transfer coefficient was evaluated to be in the range of 0.001 to 0.002 kg/s.

*The Gas Transportation Vehicle*

Figure 5 shows an embodiment of a gas transportation system 51. The system 51 includes a truck 52 having a series of metal containers (30a,30b,30c,30d,30e) mounted thereon. The metal containers (30a,30b,30c,30d,30e) are the same design as the metal container 30 of Fig. 4. The metal containers (30a,30b,30c,30d,30e) accordingly have adsorption cylinders having the ACF adsorbent material disclosed in Example 1 above.

The system 51 can be used to store ammonia gas in the metal containers (30a,30b,30c,30d,30e) and transport it from point to point.

The conduits (22A,22B,22C,22C,22E) of the respective metal containers (30a,30b,30c,30d,30e) are connected to a common outlet conduit in the form of flexible outlet hose 42, which is in fluid communication with the outlet 40. The outlet 40 is connected to a flexible hose fitted with a funnel shaped gas outlet (44) that is located at the rear of the truck 52.

The conduits (22A,22B,22C,22C,22E) of the respective metal containers(30a,30b,30c,30d,30e) are connected to a common inlet conduit in the form of inlet passage 41, which is in fluid communication with the gas inlet 38. The gas inlet 38 is connected to a flexible hose 43 fitted with a funnel shaped gas inlet 50 that is located at the rear of the truck 52.

The truck 52 is also provided with a generator (46) to supply power during the adsorption and desorption cycles. The truck 52 also includes a blower (54) to induce a draft inside the metal container 30 so as to manipulate the pressure within the metal container to either adsorption conditions or desorption conditions. The truck 52 is also provided with a control system (not shown) for controlling the desired operation of any of

the metal containers (30a,30b,30c,30d,30e) to enable adsorption or desorption of gas in use. Operation of the control system may be located in the cabin of the truck 52.

It will be appreciated that in use, the control system of the truck, creates adsorption conditions within the metal container to allow gas to adsorb onto the ACF. via the sides of the mesh cylinders. . The inlet 38 is connected to a gas source and passes the gas under pressure, through the common gas inlet 41 where it enters the metal chambers (30a, 30b,30c,30d,30e) through the outer cylindrical mesh of the corresponding mesh cylinders located inside the metal chambers (30a, 30b,30c,30d,30e). Gas is adsorbed and thereby stored on the ACF. This means that the truck 52 is capable of transporting the stored gas to one or more locations.

When the gas is to be released from the metal container, the controller controls the pressure of the gas within the metal container 30 to desorption conditions (that is a pressure at which desorption from the ACF occurs). This means that gas desorbs from the ACF and thereby reports to the conduits (22A,22B22C,22D, 22E) of the respective metal containers(30a,30b,30c,30d,30e). The top of each conduit (22A,22B,22C,22D,22E) passes the gas to the outlet conduit 44. Accordingly, the vehicle can advantageously be used to transport and store gas such as ammonia from different locales.

*Design of ammonia storage system on vehicle*

Table 1 shows an exemplary design specifications of an ammonia storage system (gas or liquid ammonia) on a vehicle as described above, for a 4 $m^3$ storage tank that has capable of storing 2000 kg ammonia at 85% of its capacity.

Table 1 Design Specifications

| | Liquid Ammonia Discharge | Gas discharge |
|---|---|---|
| Diameter of discharge line | 25.4 mm φ | 19 mm φ |
| Discharge rate | 56.7 litter / min | Max 50 $m^3$ / min |
| Flash rate to adsorber | 10 m3/ min as gas<br>20% vaporization of discharge liquid: due to expansion to atmosphere | 20% of stored amount:<br>due to cooling by expansion to atmosphere with accompany by decrease of inner temperature and pressure |
| Recovery | To adsorber as gas 400kg/h & to container as liquid 1600kg/h | To adsorber as gas 400kg/h |

Table 2 shows exemplary specifications of the assembly 121 described above with reference to Fig 4a and Fig 4b.

**Table 2**

| | |
|---|---|
| Adsorbent | CaCl2 impregnated ACF-1300 |
| Weight ratio CaCl2 / ACF | 40 Wt % |
| Adsorption Capacity | 0.4 kg-ammonia / kg adsorbent |
| One module<br>Outer/ inner diameter<br>Height<br>Weight | Cylindrical shape<br>700/100 mm<br>295 mm<br>20 kg |
| One Metal container (one | 100 kg |

| | |
|---|---|
| container of impregnated adsorbent) | |
| Total Weight of adsorbent | 1000 kg |
| Flow Velocity | 0.15 m/sec |
| Contact time | 2 sec |
| Cooling capacity Flow rate | 134 kW |
| Blower<br>Volume flow rate<br>Power<br>Fan static pressure | <br>5000 $m^3$/hr<br>23.8 kW<br>50 in wg |

**Ammonia Discharge Test Facility**

Fig 11 shows a schematic flow diagram of an ammonia discharge test facility 200. The testing facility comprises three ammonia cylinders (142,144,146) that store ammonia gas therein. The ammonia cylinders (142,144,146) are respectively provided with outlet conduits (162,163, 164) for the flow of gas therefrom. The outlet conduits (162,163,164) are respectively provided with butterfly valves (158, 156,154) to respectively regulate the flow of gas out of the ammonia cylinders (142,144,146). The outlet conduits (162,163,164) are connected to a common outlet conduit 162 through the butterfly valves (158, 156, 154). The ammonia cylinders (142,144,146) are also provided with respective pressure gauges (148,150,152) to measure the change in pressure of ammonia. The ammonia cylinders reside on measuring balances (not shown) to determine the weight and therefore the release of ammonia over time.

There is also provided a storage tank 160 for storing ammonia gas. The common outlet conduit 162 extends into the storage tank 160. The storage tank 160 is also provided with an outlet conduit 166 having a butterfly valve 168 for regulating the flow of gas out of the tank 160.

There is provided an assembly 121′ comprising a single train of five metal ' containers (30F,30G,30H,30I,30J). The single train assembly 121′ is identical to the assembly 121 above, except that in this assembly 121′ there is only a single train of metal container train 136′ described above with reference to Fig 4a and Fig 4b.

In this ammonia discharge test facility 200, the metal containers (30G,30H,30I) are isolated and therefore not in operation. The metal containers (30F,30J) are able to receive ammonia gas from the tank 160.

The assembly 121′ is provided with an outlet conduit 172. The outlet conduit 172 extends from the assembly 121′ to a blower 170. In use the conduit 172 transports the gas from the assembly 121′ to the blower 170.

A water cooling circuit is also provided in the assembly 121′ for transferring cooling water to and from the cooling disks 101 located in each of the operating metal containers (30F,30J) during testing. In Fig. 11, the conduits of the cooling water circuit is shown with dashed lines, while the ammonia conduit flow lines are shown with solid lines.

The cooling water circuit is also in fluid communication with a centrifugal pump 178 via an outlet conduit 188. The cooling water circuit is also provided with an outlet conduit 190 that extends from the pump 178 into a chiller 180. Two thermometeres (184,186) are provided on the conduits (190,192) respectively to measure the inlet and outlet temperatures of water flowing into and out of the chiller 180.

There is also provided four thermometers T1,T2,T3 and T4(not shown) at various positions in the metal

container 30A for measuring the temperature of the adsorbent material.

The cooling water circuit also includes conduit 192 that extends from the chiller 180 up to a flow meter 182. In use the flow meter measures the volume of water flowing out of the chiller 180. The flow meter is provided with an outlet conduit 182 that extends from the flow meter up to the assembly 121'.

There are provided two water tanks (174,176) which are in fluid communication with each other via a connecting conduit 175. The water tanks (174,176) are also in fluid communication with the blower 170.

**Ammonia Discharge Test Results**

Ammonia gas was released from the cylinders (142,144,146) by opening the valves (158,156,154) and into the storage tank 160. The ammonia gas then passed to the assembly (121') via conduit 166 and valve 168. Ammonia gas was adsorbed onto the adsorbent material provided in the metal containers (30F,30J).

Temperature readings of the thermometers (184,186,T1,T2,T3,T4) were recorded at various time points. Also the changes weight of the ammonia cylinders were recorded using the weighing balances described above to determine the amount of ammonia released to the assembly 121'.

Figure 12 shows the temperature profile of the adsorbent material enclosed in the metal container 30A of the temperature thermometers (T1,T2,T3,T4) over time. Figure 13 shows the weight profile of the ammonia cylinders (142,144,146) over time.

Table 3 summarizes the total weight of ammonia adsorbed onto the activated carbon material over time. It

was found that in a total of 38.3 kg ammonia was adsorbed which corresponds to 19% of discharged ammonia from the ammonia cylinders (142,144,146) during the testing time.

**Table 3**

**Total adsorbed weight on adsorption mesh cylinders**

| Cylinder | 142 | 144 | 146 |
|---|---|---|---|
| Initial weight, kg | 120.6 | 111.7 | 128.4 |
| Final weight, kg | 108.6 | 100.0 | 113.8 |
| Adsorbed Weight, kg | 12.0 | 11.7 | 14.6 |

Table 4 shows a comparison of the predicted and experimental adsorption heat during the test. For instance, for cylinder 144, theoretically evaluated average heat release was 14.4kW based on adsorption heat of 1078 kJ/kg, release period of 10 min and weight of 8 kg:

$$8\text{kg} \times 1078\ \text{kJ}/(10\ \text{min} \times 60\ \text{sec}) = 14.4\ \text{kW}$$

The experimental value of adsorption heat was obtained by the temperature difference between inlet and outlet temperature of water flowing into and out of the chiller 180 multiplied by the flow rate.

**Table 5**

**Comparison of predicted and experimental adsorption heat**

| Ammonia cylinder | 1 | 2 | 3 |
|---|---|---|---|
| Experimental value (kW) | 12.8 | 12.8 | 18.0 |
| Predicted value (kW) | 9.1 | 14.4 | 14.7 |

It has been demonstrated in the test and as shown by Table 5 that most of the heat of adsorption was removed by the cooling water. The test confirmed that the assembly 121' disclosed herein is safe for ammonia storage and transport.

**Applications**

Advantageously it will also be appreciated that because at least some methanol is rinsed from the ACF, the concentration of methanol in the ACF is lower during the $CaCl_2$ impregnation step. This means that the $CaCl_2$ impregnation step can be conducted at higher temperatures and pressures with a significantly reduce risk of explosion or fire by the methanol.

An advantage of the disclosed embodiments is a simple method that provides improved impregnation of the salts and scalability to large-scale applications.

Another advantage of the embodiments of the disclosed embodiments is the high adsorption capacity of the material. The ACF adsorbent posses superior adsorption capacity and workability. The adsorbent material can be easily shaped into various forms. For example the material can be easily used to produce adsorption cells (fig 2). The material provides higher surface area per unit volume for adsorption of a gas.

It has surprisingly been found that pre-treatment of the activated carbon material with a polar organic solvent provides improved impregnation of activated carbon material.

It should be realized that the disclosed embodiments of the adsorbent material can be used for adsorbing gases other than ammonia, such as hydrogen sulfide, sulfur dioxide, hydrogen chloride, chlorine, nitrogen oxide such as NOx, etc.

The disclosed embodiments of the adsorbent material provide a useful and safe alternative to high pressure gas storage of ammonia. Accordingly, the adsorbent material may be used in the metal container 30 and is

therefore particularly useful when used to transport the ammonia gas.

There is a need to provide adsorbent materials that overcome or at least ameliorate one or more of the disadvantages described above. There is a need of adsorbent materials that can adsorb gases reversibly, posses higher adsorption capacities and facilitate adsorption and de-sorption process.

It will be apparent that various other modifications and adaptations of the invention will be obvious to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention. It is intended that all such modifications and adaptations come within the scope of the appended claims.

## Claims

1. A method of producing an adsorbent material capable of adsorbing fluid, the method comprising the step of exposing an activated carbon material to a polar organic solvent before impregnating the activated carbon material with a salt.

2. A method as claimed in claim 1, comprising the step of removing at least a portion of the polar organic solvent from the activated carbon material.

3. A method as claimed in claim 2, comprising the step of introducing the salt to the activated carbon material in the presence of an aqueous solution.

4. A method as claimed in claim 3, comprising the step of removing the aqueous solution from the activated carbon material.

5. A method according to claim 4, comprising calcinating the adsorbent material.

6. A method according to claim 1, comprising selecting the activated carbon material from the group consisting of carbon granules, carbon fibers, carbon nano-fiber, graphite material, carbon matrix, carbon powder, carbon felt and mixtures thereof.

7. A method according to claims 1, comprising selecting a low carbon polar organic solvent as the polar organic solvent.

8. A method according to claim 1, comprising selecting the polar organic solvent from the group consisting of alcohols, ethers, aldehydes, ketones, carboxylic acids and mixtures thereof.

9. A method according to claim 1, comprising selecting a low carbon alcohol as the polar organic solvent.

10. A method according to claim 9, wherein the low carbon alcohol is selected from the group consisting of: methanol, ethanol, propanol, butnaol, pentanol and mixtures thereof.

11. A method according to claim 1, comprising selecting a metal halide as the salt.

12. A method according to claim 11, comprising selecting the metal of the metal halide from the group consisting of group IA metals, group IIA metals and group VIII metals of the Periodic Table of elements, and mixtures thereof.

13. A method according to claim 11, comprising selecting the halide of the metal halide from the group consisting of fluoride, bromide, chloride, iodide and mixtures thereof.

14. A method according to claim 1, comprising undertaking the exposing at a temperature in the range selected from the group consisting of about $10^0$C to about $80^0$C, about $15^0$C to about $50^0$C, about $15^0$C to about $40^0$C, about $15^0$C to about $30^0$C, about $20^0$C to about $30^0$C.

15. A method according to claim 1, comprising undertaking the exposing at a pressure in the range selected from the group consisting of about 0.5 bar to about 4 bar, 0.8 bar to about 3, about 0.9 bar to about 2, and about 0.9 bar to about 1.1.

16. A method according to claim 5 comprising undertaking the calcinating at a temperature in the range selected from the group consisting of about 100$^0$C to about 500$^0$C, about 150$^0$C to about 450$^0$C, about 200$^0$C to about 400$^0$C, about 300$^0$C to about 400$^0$C, about 120$^0$C to about 300$^0$C, about 150$^0$C to about 250$^0$C, and about 150$^0$C to about 200$^0$C.

17. An adsorbent material made in a method according to claim 1.

18. Use of an adsorbent material made in a method according to claim 1, for adsorption of a fluid.

19. Use of an adsorbent material according to claim 18, wherein the fluid contains atoms selected from the group consisting of Nitrogen(N), Oxygen (O), sulfur (S), Hydrogen (H), Chlorine (Cl), fluorine (F), carbon (C) and combinations thereof.

20. Use according to claim 18, wherein the fluid is ammonia gas or liquid ammonia.

21. An apparatus for storing fluid comprising:

a housing having a chamber for enclosing adsorbent material therein, the adsorbent material comprising an activated carbon impregnated with a salt; and

at least one conduit extending through the housing and into the chamber for transfer of fluid to and from the chamber.

22. An apparatus according to claim 21, wherein the adsorbent material is made in a method according to claim 1.

23. An apparatus for storing fluid comprising:

a housing having a chamber for locating a fluid adsorbent material therein;

at least one conduit extending through the housing and into the chamber for transfer of fluid to and from the chamber; and

a heat exchanger for driving adsorption of fluid onto the fluid adsorbent material or for driving desorption of fluid from the fluid adsorbent material, or both.

24. A vehicle for transporting fluid comprising:

a housing having a chamber for locating a fluid adsorbent material therein; and

at least one conduit extending through the housing and into the chamber for transfer of fluid to the chamber or from the chamber, or both.

25. A vehicle according to claim 24, wherein the vehicle is a self-propelled vehicle.

26. A vehicle according to claim 24, comprising a heat exchanger for driving adsorption of fluid onto the fluid adsorbent material or for driving desorption of fluid from the fluid adsorbent material, or both.

27. A vehicle according to claim 26, wherein the heat exchanger is located within the housing.

28. A vehicle according to claim 24, comprising a fluid pump for moving fluid to and from the chamber.

29. A vehicle according to claim 28, wherein the fluid pump comprises a blower for moving gas to and from the chamber.

30. A vehicle according to claim 24, comprising a plurality of housings, wherein the chambers of said plurality of housings are capable of being in fluid communication with each other.

31. A vehicle according to claim 24, wherein the fluid adsorbent material is made in a method according to claim 1.