

Hydrogen Storage Unit

Field of the invention

The invention relates to a hydrogen storage unit and particularly a unit which can be used for solid metal hydride absorption/adsorption and desorption of hydrogen.

Background of the invention

Hydrogen may be stored for use as a fuel or for other purposes. Some hydrogen storage units include an enclosed volume carrying a bed of hydrogen storage material such as catalysed MgH_2 or other high temperature metal hydride (and various alloys).

There are a number of thermal challenges associated with such storage units. Typical hydrogen storage materials must be held within a narrow band of operating temperatures in the vicinity of 365°C to operate effectively.

Typically, a temperature gradient of less than 20°C is required within the bed of a hydrogen storage material during absorption/adsorption in order to ensure all the material absorbs/adsorbs the full amount of hydrogen it is chemically capable of. If the temperature of the coldest material is more than 20°C below the temperature of the hottest material in the bed, the catalyst will chemically react with the hydrogen to form a hydride, thereby decreasing its effectiveness. If this temperature difference is significantly more than 20°C , as commonly occurs with the material closest the outer wall, the resulting kinetics will be substantially slowed and the absorption/adsorption will not proceed to completion in a practical time.

As the storage unit is filled, hydrogen is absorbed/adsorbed by the hydrogen storage material. This reaction is exothermic, i.e. gives off heat. The heat of reaction adds to the heat of compression and must be dissipated in order to hold the hydrogen storage material within the desired operating temperature range.

As the storage unit is emptied, i.e. when delivering hydrogen, hydrogen is desorbed from the hydrogen storage material. This reaction is endothermic, i.e. absorbs heat.

Some storage units incorporate a heater to maintain the hydrogen storage material within the desired operating range of temperatures while the storage unit is delivering hydrogen. As the desirable operating temperature is typically well above the ambient temperature, it is desirable to minimise heat losses from the storage unit to the ambient environment to minimise the energy input required from the heater, i.e. maximise the thermal efficiency.

Hydrogen storage materials produce stress and can deform or destroy the vessel because the material expands when it absorbs/adsorbs hydrogen. Stress accumulation can also occur in hydride beds at high packing densities as a result of the finely pulverised particles falling in to gaps at the bottom of the vessel, thus causing the hydride packing fraction at the bottom of the vessel to gradually increase.

Figure 1 schematically illustrates a cross section of a prior art hydrogen storage unit 10 in the form of a tank including an outer wall 14 containing a bed 12 of hydrogen storage material in the form of hydride. The outer wall 14 is mechanically stressed by a net outward force F_R . The net outward force F_R is equal to the force of expansion (i.e. mechanical stress generated by the hydride) plus the hydrostatic force (i.e. the pressure of the hydrogen).

Figure 2 illustrates an approach of the prior art to minimising the temperature gradient in the metal hydride bed. Figure 2 is an axial cross section view illustrating an outer vessel 20 thermally insulated by layer 30 about its exterior.

The outer vessel 20 carries aluminium foam 18, dividers 32 and metal hydride particles 34. The metal hydride particles fill the void spaces of the aluminium foam 18. The mixture of the aluminium foam 18 and the metal hydride particles 34 desirably has a higher thermal conductivity than a solid bed of metal hydride particles. The dividers 32 extend transversely across, and are spaced longitudinally along, the outer vessel 20 to minimise the movement of the metal hydride particles 34 (which is typically in the form of a pulverised powder) to eliminate dense spots. The dividers 32 minimise the distance the metal hydride particles 34 can travel.

A line 22 extends longitudinally within the interior of the outer vessel 20. The line 22 is a tubular structure with gas permeable walls forming a porous metal filter.

Line 22 thereby fluidly communicates with the interior of the outer vessel 20 to define reversible flow path 24 through which hydrogen is received into, and delivered from, the interior of the outer vessel 20. Desirably the line 22 is positioned above an upper extent of the metal hydride particles 34.

The storage unit 16 includes a cooling tube 28 in the form of a U shaped loop extending within the interior of the outer vessel 20 along the full length of the storage unit 16. The cooling tube 28 includes an inlet 26 and an outlet 25. Coolant is received into the tube 28 via the inlet 26 and absorbs heat from the aluminium foam 18 and metal hydride particles 34 as it traverses the interior of the outer vessel 20 before emerging from the outlet 25.

Figure 3 illustrates a transverse cross section view of the prior art storage unit 16 of Figure 2.

These various constructions of the prior art have significant drawbacks.

Aluminium foam is very expensive. It typically costs at least three times as much as the metal hydride. Moreover, the utilisation of the aluminium foam requires the metal hydride be in fine powder form so as to effectively fill the pores of the foam and achieve high packing densities. Production of fine powder significantly increases the material production cost due to increased tooling demands.

Dividers can reduce the stress on the wall of the cylinder but do not eliminate it. The resulting stress on the wall of the cylinder with dividers can still far exceed the hydrostatic stress exerted by the gaseous hydrogen. Therefore, the cylinder walls need to be much thicker than other storage tanks to resist such force.

The drawback of using a heavily insulated cylinder with internal heat exchanger for removing heat is the cost of safe heat transfer fluids for extracting the heat at, say, 350°C. The available fluids are typically expensive, auto ignitable in air and highly toxic.

On top of this, the working temperature of the available fluids is typically limited to 400°C which relates to a limited desorption pressure of 3 to 5bar which in turn limits the rate at which hydrogen may be delivered from the unit. To achieve higher pressure desorption in high temp hydrides, significantly higher temperatures are required. Temperatures up to 600°C and beyond are achievable with electric heater elements.

The above reference to the prior art is not intended to be an admission that the information forms part of the common general knowledge of a person skilled in the art.

Summary of the invention

One aspect of the invention provides a hydrogen storage unit including:

- a fluid communication port ;

- an outer vessel wall; and

- an inner compartment for hydrogen storage material in fluid communication with the fluid communication port, the inner compartment being spaced from the outer vessel wall to define a peripheral volume between the inner compartment and outer vessel wall.

In a preferred form of the invention, the inner compartment is in fluid communication with the peripheral volume and the fluid communication port includes one or more flow paths for fluidly communicating the inner compartment with the exterior of the storage unit to deliver hydrogen from, and receive hydrogen in to, the hydrogen storage unit. The flow communication port is configured to at least substantially bypass the peripheral volume during desorption of hydrogen. During delivery, the hydrogen in the peripheral volume is preferably static or slow moving to insulate the hydrogen storage material from the exterior.

It is desirable that the outer vessel wall be substantially mechanically isolated from mechanical stresses generated by hydrogen storage material contained within the inner compartment. Further it is desirable to isolate the vessel from thermal expansion or

contraction stresses that may be induced by temperature differentials that occur during cycling of the hydride.

The inner compartment of the storage unit is constructed to contain hydrogen storage material. According to such units, the outer vessel may surround at least a substantial portion or totally contain the inner compartment and be spaced therefrom to define the peripheral volume around the inner compartment. The inner compartment may include a compartment wall and end pieces, the end pieces engaging the outer vessel wall to support the inner compartment within the outer vessel. The compartment wall is preferably cylindrical and the end pieces conical, frusto-conical or hemispherical in shape. By supporting the inner compartment at the end pieces, intermediate structural components between the inner compartment and the outer vessel can be avoided thus reducing or eliminating heat conduction pathways between the hydrogen storage material in the inner compartment, the outer vessel and the ambient outer environment.

Optionally, the inner compartment wall is substantially cylindrical and the outer vessel wall totally encloses the inner compartment. The outer vessel may include a substantially cylindrical interior wall concentrically surrounding the inner compartment defining the peripheral volume which is an annular space. Preferably the inner compartment is supported within the outer vessel at the end pieces only. Thus there are no structural supports between the outer vessel wall and the inner compartment wall and hence no direct path through structural supports for heat conduction. In one form of the invention, the inner compartment fluidly communicates with the peripheral volume around the inner compartment during receipt of hydrogen so that the peripheral volume is pressurised. The inner compartment fluidly communicates with the peripheral volume at a location proximal to the fluid communication port and preferably through the end pieces. The fluid communication may be provided by gas equalisation ports in the end pieces of the inner compartment.

According to another form of the invention, the peripheral volume is fluidly isolated from the inner compartment. A fluid pressure device may be provided to control the pressure within the peripheral volume. By way of example, the fluid pressure device may be

configured or controlled to evacuate the peripheral volume during said delivery of hydrogen.

The inner compartment may be predominantly formed of sheet metal such as 0.75 millimetre thick stainless steel (or other hydrogen compatible materials i.e. copper, aluminium etc).

The hydrogen storage material may include one or more high temperature metal hydrides.

A heating element may be provided to heat the hydrogen storage material during said delivery of hydrogen.

A second aspect of the invention provides a hydrogen storage unit including:

- a fluid communication port;

- an inner compartment for containing a hydrogen storage material;

- an outer vessel wall surrounding the inner compartment to define a peripheral volume about the inner compartment isolated from the inner compartment;

- a fluid pressure device in communication with the peripheral volume; and

- a controller for controlling the fluid pressure device;

wherein the controller is configured to:

- i) reduce the pressure in the peripheral volume during desorption of hydrogen to insulate the inner compartment; and

- ii) increase the pressure in the peripheral volume during absorption/adsorption of hydrogen to conduct heat from the inner compartment to the outer vessel wall.

A third aspect of the invention provides a hydrogen storage unit consistent with the first aspect wherein:

the inner compartment is connected to the peripheral volume by at least one pressure equalising port; and

the fluid communication port fluidly communicates with the inner compartment bypassing the peripheral volume;

As with the first aspect, in the second and third aspects, the inner compartment may include a compartment wall and end pieces, the end pieces engaging the outer vessel wall to support the inner compartment within the outer vessel. The compartment wall is preferably cylindrical and the end pieces conical or frusto-conical in shape. By supporting the inner compartment at the end pieces, intermediate structural components between the inner compartment and the outer vessel can be avoided thus reducing or eliminating heat conduction pathways between the hydrogen storage material in the inner compartment, the outer vessel and the ambient outer environment.

The fluid communication port enters the outer vessel at the top of the hydrogen storage vessel and passes through an aperture in the top end piece of the inner compartment.

Brief description of the drawings

Figure 1 is a schematic transverse cross section view of a hydrogen storage unit;

Figure 2 is an axial cross section view of a hydrogen storage unit;

Figure 3 is a transverse cross section view of the hydrogen storage unit of Figure 2;

Figure 4 is a side view of a hydrogen storage unit in accordance with an embodiment of the invention;

Figure 5 is an axial cross section view of the hydrogen storage unit of Figure 4;

Figure 6 is a close up view of an end portion of the axial cross section illustrated in Figure 5;

Figure 7 is a schematic transverse cross section view of a hydrogen storage unit in accordance with another embodiment of the invention;

Figure 8 is a FEA simulation of hydrogen storage unit (a) without and (b) with hydrogen gap; and

Figure 9 is a FEA simulation of hydrogen storage unit showing heat flux with (a) 7 bar hydrogen in the gap for an absorption/adsorption, and (b) 1 bar hydrogen in the gap for a desorption.

Detailed description of the embodiments

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

Figures 4, 5 and 6 illustrate a preferred embodiment of the invention. The hydrogen storage unit 50 includes an outer vessel wall 52A carrying an inner compartment 54A which in turn carries a body of hydrogen storage material 56 preferably in the form of MgH_2 . A tubular neck 58 defines a fluid communication port for an inlet/outlet flow path communicating with hydrogen storage material 56 carried in the inner compartment 54A.

The outer vessel wall 52A is substantially cylindrical and terminates in outwardly domed ends 62 and 64. An electrical junction box 51 is carried by domed end 64. The hydrogen storage vessels generally stand upright on base 57 including supports 72 and junction box 51 for the connection of electrical power to electrical heating elements 55. The heating elements extend from the junction box 51 but only that part of the elements contained within the inner compartment is active and provides heat.

The inner compartment 54A is also cylindrical and sits concentrically within the outer vessel 52A. The exterior of the inner compartment 54A is about 3mm smaller (in radius) than the inner surface of the outer vessel wall 52A to define a peripheral volume 60 in the form of an annular gas space which is about 3mm thick. In this embodiment, the peripheral volume 60 is filled with hydrogen and thus forms a hydrogen gap.

The inner compartment allows for the thermal expansion and contraction of the hydrogen storage material independent of the outer vessel wall. This reduces the levels of thermally induced stresses experienced by the outer vessel and reduces the likelihood of structural failure of the outer vessel.

Figure 7 schematically illustrates some of the advantages of this construction. The peripheral volume 60' mechanically isolates the inner wall 54' from the outer wall 52' such that the inner wall 54' experiences a net outward expansion force equal to the mechanical forces generated by expansion of the hydrogen storage material. This stress is not transferred to the outer wall 52' so that the outer wall 52' experiences a net outward force equal to the hydrostatic pressure.

The inner compartment 54A includes an inner compartment wall 54 and end pieces 66, 68. The end pieces 66, 68 engage the outer vessel wall to support the inner compartment within the outer vessel. The engagement can be either directly onto the inner dome end piece 62 or via a connection to the fluid communication port which in turn is secured to the domed end piece 62.

The compartment wall is preferably cylindrical and the compartment end pieces conical or frusto-conical in shape. By supporting the inner compartment at the compartment end pieces, intermediate structural components between the inner compartment and the outer vessel are not required thus reducing or eliminating heat conduction pathways between the hydrogen storage material in the inner compartment 54A, the outer vessel 71 and the ambient outer environment.

As illustrated the outer vessel wall 52A encapsulates substantially all of the compartment 54A.

The fluid communication conduit 58A from fluid communication port 58 enters the outer vessel at the top of the hydrogen storage vessel and passes through an aperture in the top end piece 62 of the inner compartment. The fluid communication conduit 58A communicates directly with an interior of the compartment 54A whereby hydrogen can be received into or delivered from the storage unit 50 with only minimal disturbance of the hydrogen carried in the peripheral volume 60.

In this embodiment the top compartment end piece 66, which defines an end of the inner compartment 54A to which the fluid communication conduit 58A is communicated, includes pressure equalisation ports in the form of six small apertures 70 equally spaced on a pitch circle concentric to conduit 58A. As illustrated, the apertures 70 are proximal to the neck 58.

During the removal of hydrogen from the hydrogen storage unit 50 (desorption), the hydrogen storage material is heated by heating elements in the inner compartment. Thus when the fluid communication port 58 is opened, hydrogen flows out of unit 50, from the inner compartment 54A. The peripheral volume 60 communicates with the inner compartment 54A via the apertures 70 so that pressure in the peripheral volume 60 is reduced.

The skilled person will appreciate that when the fluid communication port 58 is first opened to remove hydrogen, and the hydrogen storage material heated to desorb hydrogen, there may be an initial flow of hydrogen from the peripheral volume 60, through the aperture 70, towards the outlet 50 but thereafter during removal/desorption, the hydrogen in the peripheral volume is more or less static. This peripheral volume of low pressure hydrogen has been found to be an effective insulator useful for insulating the hydrogen storage material 56 from the outer vessel wall 52 and the exterior of the unit. This is useful for reducing heat loss during hydrogen removal/desorption and reducing the amount of heat which needs to be supplied by heating elements 55.

The unit 50 is filled by supplying hydrogen at pressure to the fluid communication port 58 whereby the hydrogen is received into the inner compartment 54A. The received hydrogen is absorbed/adsorbed by the hydrogen storage material 56. As the

absorption/adsorption of hydrogen is exothermic, during receiving/absorption/adsorption the unit 50 is heated by the heat of reaction as the hydrogen storage material 56 absorbs/adsorbs the hydrogen. As discussed, it is important that this heat is dissipated so that the hydrogen storage material 56 is maintained within its effective operating temperature range.

According to the illustrated embodiment, as hydrogen is provided at pressure into the vessel 50 through the fluid communication port 58, hydrogen flows from the inner compartment 54A and into the peripheral volume 60 via the apertures 70. As such, during receiving/absorption/adsorption the peripheral volume 60 is occupied by dense pressurised hydrogen which forms an effective heat conductor. Thus during receiving/absorption/adsorption, the peripheral volume effectively conducts heat from the hydrogen storage material 56 to the outer vessel 52 and in turn its exterior to dissipate heat.

Of course the apertures 70 are not essential. According to another embodiment of the invention, the peripheral volume 60 is fluidly isolated from the inner compartment 54A so that the peripheral volume 60 and the inner compartment 54A may be held at different pressures. According to this embodiment, as illustrated in Figure 9, a fluid pressure device, such as a positive displacement compressor, may be used to control the pressure within the peripheral volume 60'. A controller 74 is configured to drive the fluid pressure device 73 to control the pressure within the peripheral volume 60' to achieve the desired degree of insulation. By way of example, the controller 74 and fluid pressure device 73 might reduce the pressure in the peripheral volume 60' during removal/desorption for improved insulation and reduced heat losses. Indeed the fluid pressure devices 73 and controller 74 may be configured to evacuate the peripheral volume for improved insulation, i.e. by providing a negative pressure. The fluid pressure device 73 and the controller 74 may be integrated. Alternatively they may be separated by some distance. The controller 74 may be mounted within the junction box 51.

During receiving/absorption/adsorption the fluid pressure device 73 and controller 74 will typically increase the pressure within the peripheral volume 60' for improved heat transfer.

Variants of the invention have application to:

- solid-state, hydrogen cylinder packs for replacement of compressed gas MCP's;
- solid state hydrogen storage system packaged in a shipping container;
- solid state hydrogen storage system for interface to high temp fuel cell for waste heat recovery;
- hydrogen storage system to interface to internal combustion engine for waste heat utilisation;
- hydrogen storage systems for refuelling applications; and
- hydrogen storage systems for PEM fuel cell applications.

To illustrate the effectiveness of the invention, Figure 8 shows a finite element analysis simulation of hydrogen storage unit without (A) and with (B) hydrogen gap. The chilling effect is clearly noticeable on the unit without the air gap in the material closest to the outer wall. In contrast, the chilling effect in the unit with the hydrogen gap is significantly less.

The thin gap also allows a large temperature difference between the edge of the hydride bed and the cylinder wall. This allows the hydride bed to operate with $<20^{\circ}\text{C}$ temperature gradient from the centre to the perimeter (e.g. $T_{\text{center}} = 370^{\circ}\text{C}$, $T_{\text{inner wall}} = 360^{\circ}\text{C}$) while the outer wall operates at a much lower temperature of 250°C .

Lastly, the hydrogen pressure within the gap can be changed between absorption/adsorption and desorption to bias the heat transfer to match the requirements. For absorption/adsorption, where good heat transfer between the bed and the wall is required, the hydrogen pressure should be high to increase conductivity. In contrast, during desorption where heat loss is undesirable, the pressure can be much lower or a vacuum to minimise the thermal conductivity between the bed and the outer wall. The effect of hydrogen pressure in the gap is shown in Figure 9 which is a finite

element analysis simulation of hydrogen storage unit showing the much greater heat flux with (a) 7 bar hydrogen in the gap for an absorption/adsorption, and (b) 1 bar hydrogen in the gap for a desorption

A hydrogen filled gap between the bed and the wall is naturally pressurised during absorption/adsorption when higher pressures are desirable. The higher pressure hydrogen conducts heat well from the bed to the outer wall of the unit where the external cooling system can extract the heat.

A hydrogen filled gap between the bed and the wall is naturally depressurised or even vacuumed during desorption when lower pressures are desirable. The lower pressure hydrogen/vacuum insulates heat well from the bed to the wall of the unit thereby minimising heat loss.

The pressurisation and depressurisation of the gap can be passive and follow the pressure changes of the unit for absorption/adsorption and desorption. Alternatively, the gap can be isolated from the metal hydride bed and therefore have a different pressure to the bed. This would allow inducing a vacuum inside the gap while desorbing at positive pressure as well as absorbing/adsorbing at low pressure with a much higher pressure of hydrogen in the gap.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

CLAIMS

1. A hydrogen storage unit including:
 - a fluid communication port;
 - an outer vessel including an outer vessel wall; and
 - an inner compartment for hydrogen storage material in fluid communication with the fluid communication port, the inner compartment being spaced from the outer vessel wall to define a peripheral space between the inner compartment and outer vessel wall.
2. The hydrogen storage unit of claim 1 wherein the inner compartment contains the hydrogen storage material; the outer vessel surrounding at least a substantial portion of the compartment and spaced therefrom to define the peripheral volume.
3. The hydrogen storage unit of claim 2 wherein the inner compartment includes a compartment wall and end pieces, the end pieces engaging the outer vessel wall to support the inner compartment within the outer vessel.
4. The hydrogen storage unit of claim 3 wherein the inner compartment is supported in the outer vessel at the end pieces only.
5. The hydrogen storage device of claim 3 or 4 wherein the fluid communication port is configured to at least substantially bypass the peripheral volume.
6. The storage unit of claim 1, wherein the inner compartment is in fluid communication with the peripheral volume.
7. The hydrogen storage unit of claim 6 wherein the inner compartment is in fluid communication with the peripheral volume at a location proximal to the fluid communication port.

8. The hydrogen storage unit of any one of claims 1 to 7, the inner compartment being substantially cylindrical, the outer vessel surrounding substantially all of the compartment and having a substantially cylindrical interior whereby the peripheral volume is an annular space.

9. The hydrogen storage unit of any one of claim 1 to 86 wherein the hydrogen storage material includes one or more high temperature metal hydrides.

10. The hydrogen storage unit of any one of claim 1 to 7 further including at least one heating element for heating the hydrogen storage material to desorb hydrogen from the hydrogen storage material.

11. The hydrogen storage unit of claim 10 wherein the heating element includes an electric heating element.

12. A hydrogen storage unit of claim 1, wherein:

an inner compartment for hydrogen storage material in fluid communication with the fluid communication port, the inner compartment being spaced from the outer vessel wall to define a peripheral space between the inner compartment and outer vessel wall.

the peripheral volume about the inner compartment is fluidly isolated from the inner compartment; the hydrogen storage unit further including

a fluid pressure device in communication with the peripheral volume; and

a controller for controlling the fluid pressure device;

wherein the controller is configured to:

i) reduce the pressure in the peripheral volume during desorption of hydrogen to insulate the inner compartment; and

ii) increase the pressure in the peripheral volume during absorption/adsorption of hydrogen to conduct heat from the inner compartment to the outer vessel wall.

13 The hydrogen storage unit of claim 11 wherein the inner compartment includes a compartment wall and end pieces, the end pieces engaging the outer vessel wall to support the inner compartment within the outer vessel.

14. The hydrogen storage unit of claim 11 or 12 wherein the controller is configured to evacuate the peripheral volume during removal of hydrogen from the hydrogen storage unit.

15. A hydrogen storage unit of claim 1 wherein:

the inner compartment is connected to the peripheral volume by at least one pressure equalising port; and the fluid communication port fluidly communicates with the inner compartment bypassing the peripheral volume;