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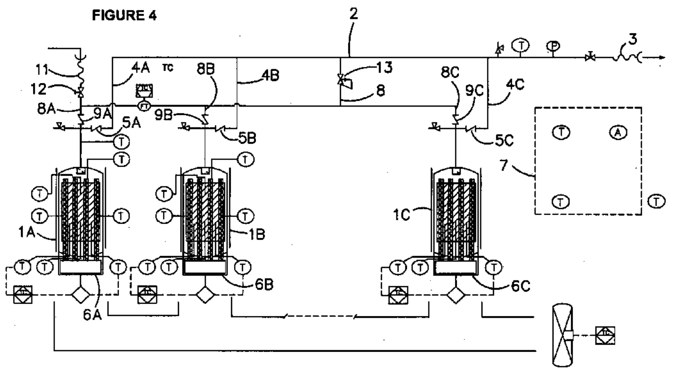
(54) Title: HYDROGEN RELEASE SYSTEM

FIGURE 4



(57) Abstract: A system for discharging hydrogen from two or more hydrogen storage vessels (1A, 1B, 1C) containing solid hydrogen storage material. The system includes at least one hydrogen supply line for connecting the hydrogen storage vessels to a hydrogen demand (3), an energy delivery system (6A, 6B, 6C) to provide heat to the hydrogen storage material in each hydrogen storage vessel to desorb hydrogen from the solid hydrogen storage material, and one or more supply connection conduits (4A, 4B, 4C) for connecting the supply line or lines to the hydrogen storage vessels (1A, 1B, 1C). Each supply connection conduit has a backflow prevention device (5A, 5B, 5C) to prevent hydrogen in the supply line from flowing back into the hydrogen storage vessels (1A, 1B, 1C). Also disclosed is a system for delivering a supply of hydrogen to a hydrogen supply line including a control system (7) to determine the timing of activation of an energy delivery system based (6A, 6B, 6C) on the hydrogen demand in the hydrogen supply line. The control system (7) activates the energy delivery system (6A, 6B, 6C) in the next hydrogen storage unit to provide a sufficient period of time for the material in the next hydrogen storage vessel to heat to the temperature at which hydrogen is provided at the supply pressure for the hydrogen supply line.

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Hydrogen Release System

Field of the invention

This invention relates to a hydrogen release system and in particular a hydrogen release system including two or more hydrogen storage vessels in which hydrogen is stored in the vessels within a hydrogen storage material.

Background of the invention

Hydrogen storage units utilising metal hydrides such as catalysed MgH_2 require temperatures above 280°C to effect a positive pressure desorption. The heat loss from a heated well insulated solid state storage cylinder with the dimensions of a commonly used G sized compressed gas cylinder can approximate 500 watts. Therefore, the heat loss from a heated 16 cylinder manifolded solid state pack can approximate 8 kilowatts. This 8 kilowatts is additional to the energy required to break the MH-hydrogen bonds and affect the adsorption. Hence the resulting thermal efficiency of such a system is extremely low resulting in increased electricity usage and poor carbon footprint.

As each storage vessel requires significant heat input to desorb hydrogen, it is advantageous to heat one vessel at a time (1) to reduce the total heating power requirement at start-up or (2) enable the desorption of hydrogen to occur at a much faster rate when a fixed amount of heating power is available. Hence, the applicant is pursuing the concept of a manifolded storage system including a multiple number of hydrogen storage vessels where only one cylinder is desorbing at a time.

Unlike a compressed gas storage unit, a solid state hydrogen storage unit containing hydrogen storage material empties under a constant pressure. In a compressed gas unit, the depth of discharge can be accurately inferred from the remaining gas pressure in the cylinder. In contrast, a solid state hydrogen storage unit will discharge from full to over 90% empty at a constant equilibrium pressure determined by the operating temperature. Once the volume of stored gas is too low to supply the flow for the required demand, the pressure in the hydrogen storage vessel will reduce quickly from the equilibrium point to zero. This is typically once the depth of discharge is beyond 90%.

Generally, when hydrogen is being desorbed from only a single vessel at a time, once the equilibrium pressure in that hydrogen storage vessel begins to drop, it is too late to start heating up the next cylinder in sequence as the time to bring the vessel to desorption pressure and temperature far exceeds the remaining supply capacity of the current near empty vessel. In order to provide a constant supply of hydrogen to meet a hydrogen demand, it is desirable that the next hydrogen storage vessel in sequence begins heating well before the constant equilibrium pressure begins to drop.

Additionally, once the active desorbing cylinder is empty, it is desirable to cool down the cylinder to minimise heat loss. However, since the hydriding/dehydriding reaction is a reversible reaction, the reaction will reverse and the hydrogen storage material will absorb hydrogen once the temperature of the hydrogen storage material drops. Figure 1 shows the absorption rate of MgH_2 as a function of temperature for a given pressure. For example, the plot of the absorption rate indicates that the reaction is in the desorption direction at temperatures above the equilibrium temperature. For temperatures below the equilibrium point the reaction is in the absorption direction. Therefore, if the cylinders are connected in parallel to a supply manifold and the next cylinder in the sequence is now supplying hydrogen by being heated to above the equilibrium temperature, the previous cylinder will absorb all of this hydrogen as it cools down below the equilibrium point leaving zero net hydrogen supply to meet the hydrogen demand.

It is desirable that the present invention provides a hydrogen storage system or supply arrangement which addresses one or more of the above problems.

Reference to any prior art in the specification is not, and should not be taken as, an acknowledgment or any form of suggestion that this prior art forms part of the common general knowledge in Australia or any other jurisdiction or that this prior art could reasonably be expected to be ascertained, understood and regarded as relevant by a person skilled in the art.

Summary of the invention

According to one aspect of the invention there is provided a system for discharging hydrogen from one or more hydrogen storage vessels, the hydrogen storage vessel or vessels containing solid hydrogen storage material, the system including:

a hydrogen supply line for connecting to a hydrogen demand;

an energy delivery system to provide heat to the hydrogen storage material in at least one of the hydrogen storage vessel to desorb hydrogen from the solid hydrogen storage material;

one or more supply connection conduits for connecting the supply line to one or more hydrogen storage vessels; wherein

each supply connection conduit connected to a hydrogen storage vessel has a backflow prevention device to prevent or limit hydrogen in the supply line from flowing back into that hydrogen storage vessel when the solid storage material is no longer desorbing hydrogen at the pressure of the supply line.

In the accordance with all aspects of the invention, preferably, when the solid storage material is no longer desorbing hydrogen at the pressure of the supply line, the energy delivery system is deactivated and no longer provides heat to the hydrogen storage vessel.

In preferred forms of the invention the backflow prevention device is a one-way valve or may simply be a shut-off valve. The provision of the backflow prevention device prevents hydrogen in the hydrogen supply line from re-entering an emptied hydrogen storage vessel in which a substantial proportion of the hydrogen has been desorbed from the hydrogen storage unit and the energy delivery system deactivated or allows the hydrogen to leak back into the exhausted hydrogen storage vessel at an intended low leakage rate. Thus, as the temperature of the hydrogen storage material drops and the hydrogen storage reaction proceeds in the direction of absorbing hydrogen, hydrogen in the hydrogen supply line is prevented from re-entering or only a limited amount allowed to re-enter the emptied hydrogen storage unit from the hydrogen supply line.

As the kinetics driving the absorption of hydrogen into the cooled hydrogen storage material will absorb all of the available hydrogen in the emptied hydrogen storage unit and create a partial vacuum in the hydrogen storage vessel. In some instances, it may be desirable for the vacuum to develop.

The invention may provide a means to fill the vacuum by either supplying gases other than hydrogen such as argon, air or nitrogen or provide hydrogen to be provided to the cooling material from an auxiliary hydrogen supply. The gases other than hydrogen may be supplied or air may be intentionally allowed to leak into the vessels as they cool.

The auxiliary hydrogen supply may be connectible to the respective emptied hydrogen storage vessel when the energy delivery system to the hydrogen storage vessel is deactivated or may alternatively be a small amount of the supplied hydrogen taken off a branch outlet to the supply and returned to the vessels.

When an auxiliary hydrogen supply is provided, an amount of hydrogen is fed into the emptied hydrogen storage unit to prevent a vacuum being created. At pressures below the operating pressure for desorbing hydrogen, the kinetics for absorbing hydrogen reduces dramatically. It is preferred that the auxiliary hydrogen supply, supply hydrogen to the emptied hydrogen storage unit to maintain the pressure in the hydrogen storage vessel at atmospheric or slightly above atmospheric pressure in order to prevent leaks forming in the hydrogen storage unit and air entering the unit.

As mentioned above, the auxiliary hydrogen supply may be an auxiliary hydrogen conduit from the supply line to at least the hydrogen storage vessel which has been deactivated. The hydrogen storage conduit preferably has a pressure control valve to supply hydrogen to the deactivated hydrogen storage vessel at a pressure lower than the pressure in the supply line and preferably at atmospheric to 2 bara (or slightly above atmospheric pressure). In one embodiment, the pressure control valve is a step down valve. Alternatively, the auxiliary hydrogen supply may be a secondary hydrogen storage cylinder such as a hydrogen gas cylinder supplying gas at a pressure of between atmospheric and two atmospheres to maintain the pressure in the deactivated hydrogen storage unit at a pressure positive to atmospheric pressure.

To further limit the amount of hydrogen reabsorbed into the cooling emptied hydrogen storage cylinder, the rate of cooling of the hydrogen storage material may be increased by improving the cooling of the emptied cylinder by either or both passive or active cooling of the cylinder. Passive cooling may take the form of removing any external insulation which may be covering the exterior of the cylinder and active cooling may involve the use of an air blower over the exterior surface of the emptied cylinder or the use of a water-cooled jacket

In another aspect of the invention there is provided a system for delivering a supply of hydrogen to a hydrogen supply line including:

one or more hydrogen storage vessels containing solid hydrogen storage material,

at least one energy delivery system to supply heat to the solid hydrogen storage material in at least one hydrogen storage vessel, the heat being sufficient to desorb hydrogen from the solid hydrogen storage material; and

a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line, the control system being configured to anticipate a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand, and activate the energy delivery system in the hydrogen storage vessel a period of time prior to the anticipated time to allow the material in the hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

The above invention may be applicable to a single hydrogen storage vessel in having an energy delivery system and control system. The control system would monitor the demand and activate the energy delivery system in response to variable which indicates that hydrogen from the hydrogen storage vessel will be required to meet the anticipated hydrogen demand.

However, in a preferred form, the above system includes two or more hydrogen storage vessels containing hydrogen storage material, the control system being configured to anticipate or determine a time when hydrogen supply from a first hydrogen storage vessels will fall below a predetermined level and activate the energy delivery system in a second hydrogen storage vessel a predetermined time prior to the anticipated or determined time to allow the material in the second hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

In the preferred form of this invention, the control system comprises a sensor which monitors a variable of hydrogen supply to the supply line and a processor which activates the energy delivery system in the next sequential hydrogen supply vessel when it determines from signals from the sensor that the hydrogen supply in the hydrogen storage vessel currently connected to the hydrogen supply line has fallen below a predetermined level.

In another aspect of the invention there is provided a method of supplying hydrogen from a hydrogen delivery system to a hydrogen supply line, the system including one or more hydrogen storage vessels containing solid hydrogen storage material, at least one energy delivery system to supply heat to the solid hydrogen storage material in at least one hydrogen storage vessel, the heat being sufficient to desorb hydrogen from the solid hydrogen storage material; and a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line.

The method includes the steps of anticipating or determining a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand, and activating the energy delivery system in the hydrogen storage vessel a period of time prior to the anticipated time to allow the material in the hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

As used herein, except where the context requires otherwise, the term "comprise" and variations of the term, such as "comprising", "comprises" and "comprised", are not intended to exclude further additives, components, integers or steps.

Brief description of the drawings / figures

Figure 1 is a graph of a typical reaction rate versus temperature curve for hydrogen absorption of a metal hydride material. The equilibrium points between absorption and desorption for a given pressure is defined by the intersection of the x-axis;

Figure 2 is a flow chart for sequential desorption of manifolded metal hydride cylinders based on digital mass flow meter integration;

Figure 3 is a flow chart for sequential desorption of manifolded metal hydride cylinders based on heater power integration;

Figure 4 is a process and instrumentation diagram showing configuration of passive gas valves;

Figure 5 is a FEA simulation of temperature profile of a cylinder cooling under 1.1 bara.; and

Figure 6 is a FEA simulation of concentration profile of a cylinder cooling under 1.1 bara.

Detailed description of the embodiments

Referring to figure 4, the connection of hydrogen storage vessels 1A, 1B, 1C is schematically shown. The hydrogen storage vessels are filled with a suitable hydrogen storage material such as MgH_2 or other hydride forming alloy which absorbs hydrogen above a predetermined temperature and pressure and desorbs hydrogen when the temperature is raised above the desorption temperature. The vessels are connected in parallel by a common desorption gas manifold 2 to a hydrogen supply line 3. The supply line 3 is generally on site where the hydrogen storage vessels are delivered to meet a hydrogen demand at the site.

A hydrogen conduit 4A, 4B, 4C is connectable to the hydrogen storage vessels !A, !B, !C respectively to receive hydrogen gas discharged from that vessel. A hydrogen storage vessel containing hydrogen storage material such as magnesium hydride discharge hydrogen under a constant pressure when heated to the absorption temperature. Hydrogen continues to be discharged until it is substantially empty at which time the discharge pressure drops dramatically.

The hydrogen discharge conduits 4A, 4B, 4C connecting to the hydrogen desorption manifold are preferably provided with backflow prevention devices 5A, 5B, 5C such as one way valves which prevent hydrogen gas in the manifold from returning to the discharge/spent/depleted hydrogen storage vessel 1A, 1B, !C respectively. As the decrease in discharge pressure from the hydrogen storage vessel occurs close to the point at which the hydrogen storage vessel is totally depleted, it is essential for the continual supply of hydrogen to the hydrogen supply line that the next hydrogen storage vessel to supply hydrogen is heated to the required desorption temperature by the time that the pressure begins to decrease in the nearly depleted hydrogen storage vessel.

A process controller 7 monitors the desorption process in the discharging hydrogen storage vessel and commences heating the next hydrogen storage vessel at an appropriate time prior to the pressure drop to ensure continuity of supply. This is done by activating heating element 6A, 6B, 6C at the appropriate time. The operation of the controller will be described in more detail later. The heating elements may be electrical heating elements which are located either internally or externally of the hydrogen storage vessels. To enhance the effects of the heating an insulated heating jacket may be provided during the heating and desorption operation. Once the hydrogen storage vessel 1A, 1B, 1C has finished discharging hydrogen, the energy source to the heating element of the hydrogen storage vessel is deactivated and the hydrogen storage material is allowed to cool. Ideally any insulated jacket may be removed when the heating elements deactivated. As illustrated in figure 1, once the hydrogen storage material cools below the equilibrium temperature (in the direction of arrow T), the kinetics for the absorption/the absorption reaction favours absorption of hydrogen. Hence all hydrogen available to the hydrogen storage material is absorbed potentially creating a negative pressure (ie. pressure below atmospheric, 1 bar absolute) in the hydrogen storage vessel.

If it is desirable to prevent pressure in the hydrogen storage vessel dropping below atmospheric pressure, an ancillary supply source communicates with the exhausted hydrogen storage vessel at least during cooling. The ancillary supply source may be provided to the supply conduit 8A, 8B, 8C through a backflow prevention device 9A, 9B, 9C such as a one way valve. The ancillary supply source may be a separate hydrogen supply 11 such as a gas cylinder through a valve 12 or it may be a branch line 8 from the absorption gas manifold. The branch line 8 is provided with a pressure control valve to step down the pressure from the absorption manifold supply pressure to a pressure that is slightly above atmospheric ie. preferably in the range of 1-2 bar absolute. While the absorption/desorption reaction is in absorption cycle during the cool down stage of the hydrogen storage material, the reaction kinetics is very slow at that pressure so only a small volume of the hydrogen is actually absorbed.

It may be acceptable to allow a vacuum to develop in the hydrogen storage vessel and so no ancillary source need be provided. Alternatively the vacuum may be filled with other gases such as argon, nitrogen or air supplied separately or air may be intentionally allowed to leak in and fill the vacuum.

To further limit the amount of hydrogen reabsorbed into the cooling emptied hydrogen storage cylinder, the rate of cooling of the hydrogen storage material may be increased by improving the cooling of the emptied cylinder by either or both passive or active cooling of the cylinder and as shown in figure 1 reduce the reaction rate of the hydrogen absorbing onto the hydrogen storage material. Passive cooling may take the form of removing any external insulation which may be covering the exterior of the cylinder and active cooling may involve the use of an air blower over the exterior surface of the emptied cylinder or the use of a water-cooled jacket

The operation of the process controller will now be described. The individual control and sequential desorption of each pressure cylinder minimises heat loss by ensuring only one cylinder is actively desorbing. An additional cylinder is pre-heated at an appropriate time to seamlessly take over the supply of hydrogen once the active cylinder empties. The remaining cylinders are stored at room temperature until required

The operation of the system can be simplified as follows

1. Cylinder A desorbing
2. Cylinder A reaches 80% depth of discharge and initiates warm-up of Cylinder B (taking 15 minutes)
3. Cylinder B begins desorbing automatically as soon as it reaches temperature. At this stage cylinder A is still not 100% empty. Cylinder A continues to desorb slowly in parallel with Cylinder B.
4. Cylinder B reaches 20% depth of discharge and initiates cool-down of cylinder A.

Therefore, at any point in time the number of hot cylinders is given as follows.

$$n = \begin{cases} 1 & DOD(Cylinder\ A) < 0.8, \\ 2 & DOD(Cylinder\ B) > 0.2 \\ 2 & DOD(Cylinder\ A) \geq 0.8,\ DOD(Cylinder\ B \leq 0.2 \end{cases}$$

Assuming a constant flow rate of hydrogen, the average number of cylinders heated at any point of time can be estimated as,

$$avg(n) = 1.4$$

The sequencer controller keeps track of the volume of hydrogen desorbed from each cylinder in order to manage the pre-heating of the next cylinder in the sequence and the cool down of the emptied cylinder. The sequencer controller can be a programmable logic controller (PLC), a personal computer (PC), or any microprocessor based embedded controller with communications capabilities. Figure 2 depicts an example software flow chart for implementation in a PLC to manage the sequencing of the cylinders.

The depth of discharge can be calculated from integration of mass flow and implemented as shown in figure 2. Alternatively, the heater power can also be used to approximate the mass flow of hydrogen and hence infer the depth of discharge.

The flow rate of hydrogen is related to the heater power by the following equation,

$$F.R.\left(\frac{kg}{h}\right) = \frac{P_{heater}(kW) - P_{losses}(kW)}{\Delta H\left(\frac{kWh}{kg}\right)}$$

The enthalpy of reaction ΔH is a chemical property of the hydride. For MgH_2,

$$\Delta H = 10.39\left(\frac{kWh}{kg}\right)$$

The depth of discharge can easily be calculated from the flow rate by subtracting the integral from the capacity of the storage unit.

$$DOD(\%) = \frac{C_{\max(kg)} - \int F.R.\left(\frac{kg}{h}\right) dt(h)}{C_{\max(kg)}} \times 100(\%)$$

In order for this to be accurate, a good estimate of the instantaneous losses is needed. The losses will be a characteristic of the storage system but will also be dependent on ambient temperature. One possible way to estimate the losses is by sampling the ambient temperature. Alternatively, the warm-up time of the cylinders will be a function of the losses and may also be used.

Figure 3 depicts an example software flow chart for implementation in a PLC to manage the sequencing of the cylinders based on heater energy.

Alternatively the depth of discharge can be approximated through observation of the metal hydride temperature and desorption pressure.

As mentioned above, the cooling down of the solid state cylinders is managed by the inclusion of two one way gas valves (9A, 9B, 9C, 5A, 5B, 5C) on each cylinder and a pressure control valve between the desorption manifold and the absorption manifold.

- The one-way valve on the desorption side of the cylinder provides an isolation means between the cooling cylinder and the desorption manifold. So, if cylinder 1A is cooling, hydrogen cannot flow backwards from the common desorption manifold 2 to the cylinder 1A. Hence, the cylinder cannot re-absorb hydrogen that is being sourced from cylinder 1B. However, cylinder 1A can still induce a vacuum by absorbing all the free gas available within the cylinder itself.

- To maintain cylinder 1A under positive pressure, the pressure control valve 13 between the desorption manifold and the absorption manifold was added. Where hydrogen is to provide the positive pressure, the valve feeds hydrogen from the desorption manifold back into the cylinder at a pressure very close to atmospheric, e.g. 1.1bara. The absorption rate at this pressure for the cooling cylinder is approximately zero and therefore only a negligible amount of hydrogen is re-absorbed during the cooling. Once the material is cooled to room temperature the absorption rate is zero.

- It may be acceptable to allow cylinder 1A to develop a vacuum and so no hydrogen would be provided or to use another gas source such as argon, nitrogen or air to balance the pressure in the cylinder created by the cooling storage material.

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.

The claims defining the invention are as follows:

1. A system for discharging hydrogen from one or more hydrogen storage vessels, the hydrogen storage vessel or vessels containing solid hydrogen storage material, the system including:

a hydrogen supply line for connecting to a hydrogen demand;

an energy delivery system to provide heat to the hydrogen storage material in at least one of the hydrogen storage vessels to desorb hydrogen from the solid hydrogen storage material;

one or more supply connection conduits for connecting the supply line to the one or more hydrogen storage vessels; wherein

each supply connection conduit connected to a hydrogen storage vessel has a backflow prevention device to prevent or limit hydrogen in the supply line from flowing back into that hydrogen storage vessel when the solid storage material is no longer desorbing hydrogen at the pressure of the supply line.

2. The system of claim 1 wherein the energy delivery system is deactivated and no longer provides heat to the hydrogen storage vessel when the solid storage material is no longer desorbing hydrogen at the pressure of the supply line.

3. The system of claim wherein the backflow prevention device is a one-way valve or a shut-off valve.

4. The system of claim 2 or 3 wherein an auxiliary hydrogen supply system is provided to supply hydrogen to the hydrogen storage vessel once the energy delivery system has been deactivated.

5. The system of claim 4 wherein the auxiliary hydrogen supply system is an auxiliary hydrogen conduit from the supply line to at least the hydrogen storage vessel which has been deactivated.

6. The system of claim 5 wherein the auxiliary hydrogen conduit has a pressure control valve to supply hydrogen to the deactivated hydrogen storage vessel at a pressure lower than the pressure in the supply line.

7. The system of claim 6 wherein the pressure control valve supplies hydrogen to the deactivated hydrogen storage vessel at a pressure slightly above atmospheric pressure.

8. The system of claim 7 wherein the pressure control valve is a step down valve.

9. The system of claim 4 wherein the auxiliary hydrogen supply system is a secondary hydrogen storage cylinder .

10. The system of claim 9 wherein the hydrogen gas cylinder supplies gas at a pressure to maintain the pressure in the deactivated hydrogen storage unit at a pressure positive to atmospheric pressure.

11. A system for delivering a supply of hydrogen to a hydrogen supply line including:

one or more hydrogen storage vessels containing solid hydrogen storage material,

at least one energy delivery system to supply heat to the solid hydrogen storage material in at least one hydrogen storage vessel, the heat being sufficient to desorb hydrogen from the solid hydrogen storage material; and

a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line, the control system being configured to anticipate or determine a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand, and activate the energy delivery system in the hydrogen storage vessel a period of time prior to the anticipated time to allow the material in the hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

12. The system of claim 11 including two or more hydrogen storage vessels containing hydrogen storage material, the control system being configured to anticipate or determine a time when hydrogen supply from a first hydrogen storage vessel will fall below a predetermined level and activate the energy delivery system in a second hydrogen storage vessel a predetermined time prior to the anticipated or determined time to allow the material in the second hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

13. The system of claim 11, wherein the control system comprises

a sensor which monitors a variable of hydrogen supply to the supply line, and

a processor which activates the energy delivery system in the hydrogen storage vessel when it determines that the hydrogen supply has fallen below a predetermined level.

14. The system of claim 12 or 13 wherein the processor deactivates the energy delivery system of one or more of the hydrogen storage vessels when the pressure of hydrogen has fallen below the pressure in the hydrogen supply line.

15. A method of supplying hydrogen from a hydrogen delivery system to a hydrogen supply line, the system including one or more hydrogen storage vessels containing solid hydrogen storage material, at least one energy delivery system to supply heat to the solid hydrogen storage material in at least one hydrogen storage vessel, the heat being sufficient to desorb hydrogen from the solid hydrogen storage material; and a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line, the method including the steps of

anticipating or determining a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand, and heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

16. The method of claim 15 further including the step of deactivating the energy delivery system and no longer providing heat to the hydrogen storage vessel when the solid storage material in the hydrogen storage vessel is no longer desorbing hydrogen at the pressure of the supply line.

AMENDED CLAIMS
received by the International Bureau on 23 June 2011 (23.06.11)

1. A system for discharging hydrogen from one or more hydrogen storage vessels, the hydrogen storage vessel or vessels containing solid hydrogen storage material, the system including:

a hydrogen supply line for connecting to a hydrogen demand;

an energy delivery system to provide heat to the hydrogen storage material in at least one of the hydrogen storage vessels to desorb hydrogen from the solid hydrogen storage material;

a process control system; wherein the process control system monitors the description process from the one or more hydrogen storage vessels; wherein the process control system regulates the delivery energy from the energy delivery system to the one or more hydrogen storage vessels;

one or more supply connection conduits for connecting the supply line to the one or more hydrogen storage vessels; wherein

each supply connection conduit connected to a hydrogen storage vessel has a backflow prevention device to prevent or limit hydrogen in the supply line from flowing back into that hydrogen storage vessel when the solid storage material is no longer desorbing hydrogen at the pressure of the supply line.

2. The system of claim 1 wherein the energy delivery system is deactivated and no longer provides heat to the hydrogen storage vessel when the solid storage material is no longer desorbing hydrogen at the pressure of the supply line.

3. The system of claim wherein the backflow prevention device is a one-way valve or a shut-off valve.

4. The system of claim 2 or 3 wherein an auxiliary hydrogen supply system is provided to supply hydrogen to the hydrogen storage vessel once the energy delivery system has been deactivated.

5. The system of claim 4 wherein the auxiliary hydrogen supply system is an auxiliary hydrogen conduit from the supply line to at least the hydrogen storage vessel which has been deactivated.

6. The system of claim 5 wherein the auxiliary hydrogen conduit has a pressure control valve to supply hydrogen to the deactivated hydrogen storage vessel at a pressure lower than the pressure in the supply line.

7. The system of claim 6 wherein the pressure control valve supplies hydrogen to the deactivated hydrogen storage vessel at a pressure slightly above atmospheric pressure.

8. The system of claim 7 wherein the pressure control valve is a step down valve.

9. The system of claim 4 wherein the auxiliary hydrogen supply system is a secondary hydrogen storage cylinder.

10. The system of claim 9 wherein the hydrogen gas cylinder supplies gas at a pressure to maintain the pressure in the deactivated hydrogen storage unit at a pressure positive to atmospheric pressure.

11. A system for delivering a supply of hydrogen to a hydrogen supply line including:

one or more hydrogen storage vessels containing solid hydrogen storage material,

at least one energy delivery system to supply heat to the solid hydrogen storage material in at least one hydrogen storage vessel, the heat being sufficient to desorb hydrogen from the solid hydrogen storage material; and a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line, the control system being configured to anticipate or determine a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand, and activate the energy delivery system in the hydrogen storage vessel a period of time prior to the anticipated time to allow the material in the hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

12. The system of claim 11 including two or more hydrogen storage vessels containing hydrogen storage material, the control system being configured to anticipate or determine a time when hydrogen supply from a first hydrogen storage vessel will fall below a predetermined level and activate the energy delivery system in a second hydrogen storage vessel a predetermined time prior to the anticipated or determined time to allow the material in the second hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

13. The system of claim 11, wherein the control system comprises

a sensor which monitors a variable of hydrogen supply to the supply line, and

a processor which activates the energy delivery system in the hydrogen storage vessel when it determines that the hydrogen supply has fallen below a predetermined level.

14. The system of claim 12 or 13 wherein the processor deactivates the energy delivery system of one or more of the hydrogen storage vessels when the pressure of hydrogen has fallen below the pressure in the hydrogen supply line.

15. A method of supplying hydrogen from a hydrogen delivery system to a hydrogen supply line, the system including one or more hydrogen storage vessels containing solid hydrogen storage material, at least one energy delivery system to supply heat to the solid hydrogen storage material in at least one hydrogen storage vessel, the heat being

sufficient to desorb hydrogen from the solid hydrogen storage material; and a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line, the method including the steps of

anticipating or determining a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand, and

activating the energy delivery system in the hydrogen storage vessel a period of time prior to the anticipated time to allow the material in the hydrogen storage vessel to heat to the temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line to meet the hydrogen demand in the supply line.

16. The method of claim 15 further including the step of deactivating the energy delivery system and no longer providing heat to the hydrogen storage vessel when the solid storage material in the hydrogen storage vessel is no longer desorbing hydrogen at the pressure of the supply line.

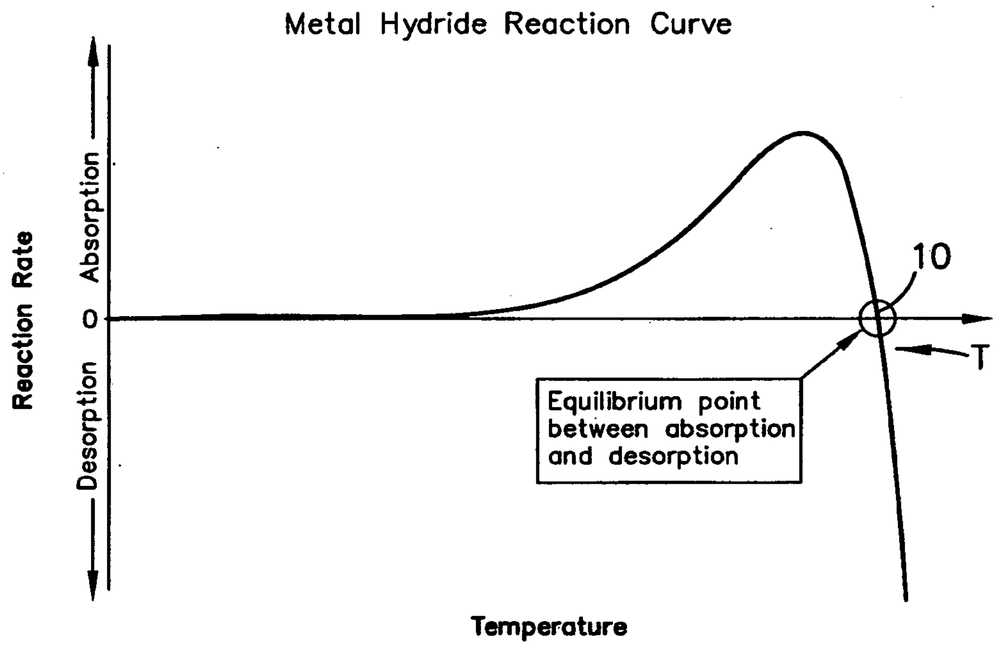
Metal Hydride Reaction Curve
Reaction Rate
Absorption
0
Desorption
10
T
Equilibrium point between absorption and desorption
Temperature

FIGURE 1

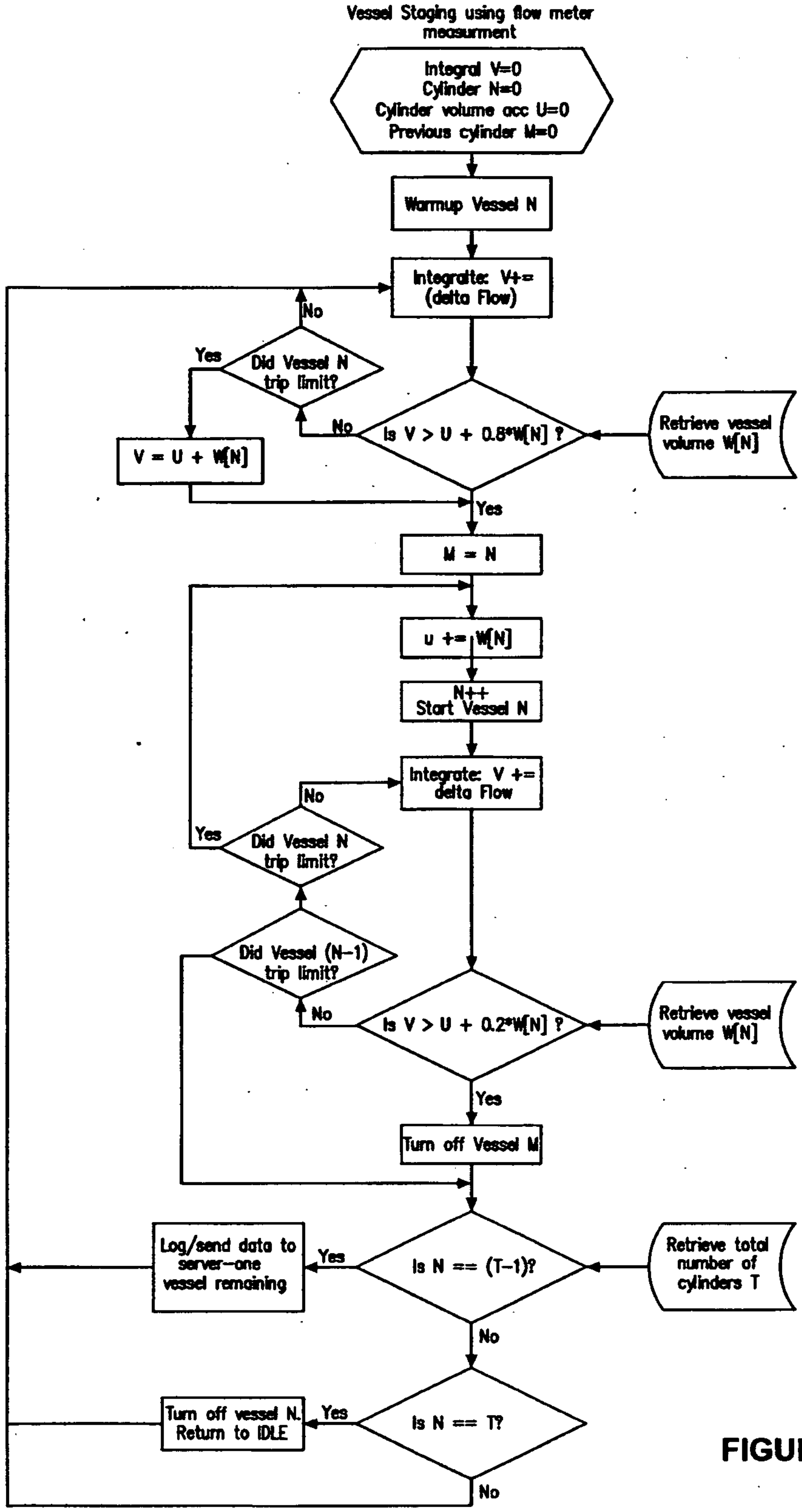
Vessel Staging using flow meter measurment
Integral V=0
Cylinder N=0
Cylinder volume acc U=0
Previous cylinder M=0
Warmup Vessel N
Integrate: V+= (delta Flow)
No
Yes
Did Vessel N trip limit?
No
Is V > U + 0.8*W[N] ?
Retrieve vessel volume W[N]
V = U + W[N]
Yes
M = N
u += W[N]
N++
Start Vessel N
Integrate: V += delta Flow
No
Yes
Did Vessel N trip limit?
Did Vessel (N-1) trip limit?
No
Is V > U + 0.2*W[N] ?
Retrieve vessel volume W[N]
Yes
Turn off Vessel M
Log/send data to server-one vessel remaining
Yes
Is N == (T-1)?
Retrieve total number of cylinders T
No
Turn off vessel N. Return to IDLE
Yes
Is N == T?
No

FIGURE 2

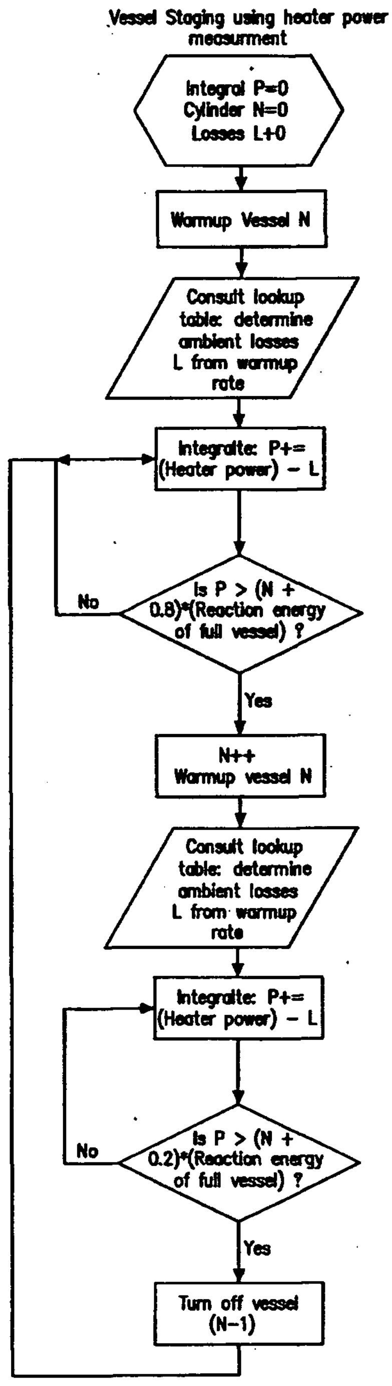
Vessel Staging using heater power measurment
Integral P=0
Cylinder N=0
Losses L+0
Warmup Vessel N
Consult lookup table: determine ambient losses L from warmup rate
Integraite: P+= (Heater power) − L
Is P > (N + 0.8)*(Reaction energy of full vessel) ?
No
Yes
N++
Warmup vessel N
Consult lookup table: determine ambient losses L from warmup rate
Integraite: P+= (Heater power) − L
Is P > (N + 0.2)*(Reaction energy of full vessel) ?
No
Yes
Turn off vessel (N−1)

FIGURE 3

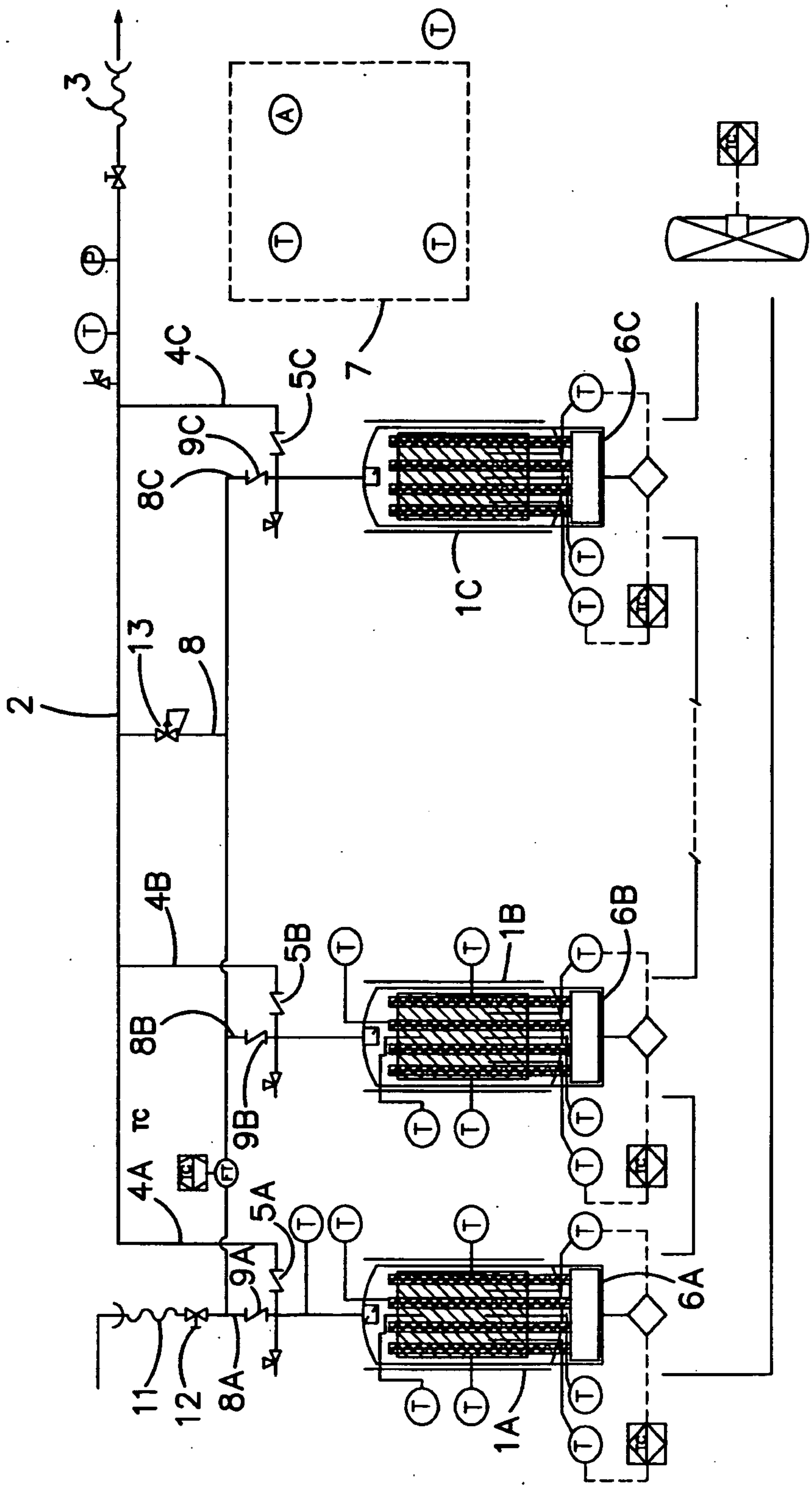

FIGURE 4

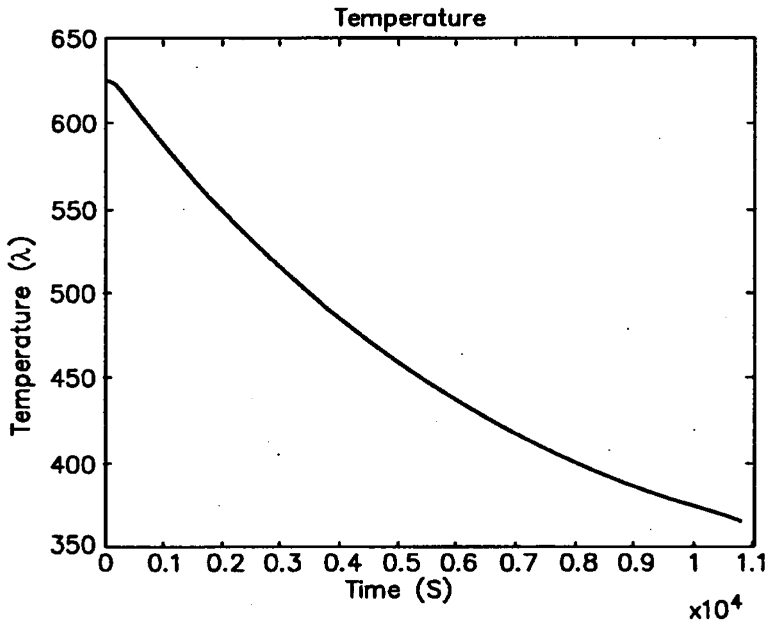

FIGURE 5

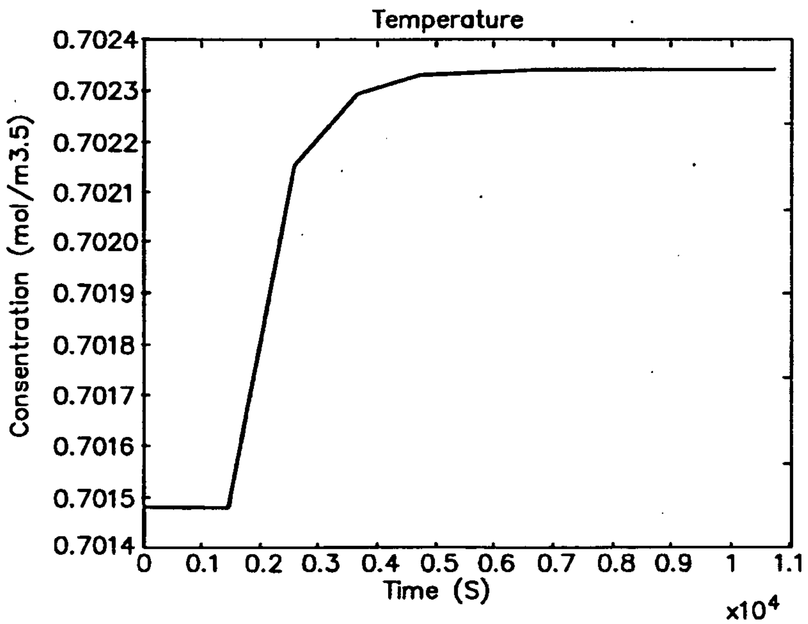

FIGURE 6

INTERNATIONAL SEARCH REPORT	International application No. PCT/AU2011/000197

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

F17C 7/00 (2006.01) ***F17C 9/04*** (2006.01) ***F17C 11/00*** (2006.01)

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)

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)

Epodoc & WPI: IPC[8]: F17C and (hydrogen and hydride and (back_flow or non_return or check or one_way))

F17C and (hydrogen and hydride and (heat+ or energy) and (control+ or activat+) and (anticipat+ or determine+)))

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 6508866 B1 (Golben) 21 January 2003 Column 4 line 35 to column 5 line 17, Claim 9, figure 2	1 and 3 2 and 4 to 10
X A	US 4402187 A (Golben et al) 6 September 1983 Column 1 line 39 to column 2 line 23, Claim 1, figures	1 and 3 2 and 4 to 10
A	US 2006/027272 A1 (Tomlinson et al) 9 February 2006 Whole Document	1 to 10
A	US 6099811 A (Stetson et al) 8 August 2000 Whole Document	11 to 16

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 31 March 2011	Date of mailing of the international search report 21 APR 2011
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **DAVID BELL** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 2309

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2011/000197

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6418275 B1 (Yang) 9 July 2002 Whole Document	11 to 16
A	US 4016836 A (M^ac^Kay et al) 12 April 1977 Whole Document	11 to 16

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplementary Sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box
(To be used when the space in any of Boxes I to IV is not sufficient)

Continuation of Box No: III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

In assessing whether there is more than one invention claimed, I have given consideration to those features which can be considered to potentially distinguish the claimed combination of features from the prior art.

This International Searching Authority has found that there are different inventions as follows:

- Claims 1 to 10 are directed to a system of discharging hydrogen from one or more hydrogen storage vessels where the hydrogen storage vessel has a backflow prevention device to prevent or limit hydrogen in the supply line from flowing back to the hydrogen storage vessel. It is considered that a backflow prevention device to prevent or limit hydrogen in the supply line from flowing back to the hydrogen storage vessel constitutes a first special technical feature and this group of claims define a first invention.

- Claims 11 to 16 are directed to a system for delivering a supply of hydrogen to a hydrogen supply line having a control system to control the timing of activation of the energy delivery system based on the hydrogen demand in the hydrogen supply line the control system being configured to anticipate or determine a time when hydrogen will need to be supplied from the hydrogen storage vessel to the hydrogen supply line to meet the hydrogen demand. It is considered that activating the energy delivery system in the hydrogen storage vessel a period of time prior to the anticipated time to allow the material in the hydrogen storage vessel to heat to a temperature at which hydrogen can be supplied at the supply pressure of the hydrogen supply line constitutes a second special technical feature and this group of claims define a second invention.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

None of the abovementioned groups of claims share any special technical feature. Because there is no common special technical feature it follows that there is no technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention *a priori*.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2011/000197**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	6508866	NONE					
US	4402187	CA	1182985	EP	0094202	JP	58217782
US	2006027272	NONE					
US	6099811	AU	45772/99	BR	9917382	CA	2375392
		EP	1203194	MX	PA01012999	WO	0079201
US	6418275	JP	2003021298				
US	4016836	DE	2640243				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX