



Rijksdienst voor Ondernemend  
Nederland

## Overzicht van patenten Thermochemische Materialen (TCM)

EOS-LT Waels

Datum            December 2008

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In opdracht van SenterNovem (nu Rijksdienst voor  
Ondernemend Nederland)

Publicatienr    RVO-158-1501/RP-DUZA  
[www.rvo.nl](http://www.rvo.nl)

Dit rapport is tot stand gekomen in opdracht van het ministerie van  
Economische Zaken.



E&I memo 2008-12

# **TCM Reactor patents**

**H.A. Zondag**

December 2008

## Summary

A large amount of detailed information is available in patents on TCM systems that have been issued over the years. This involves both system design aspects and material characteristics.

- With respect to the design aspects, all powder related patents were focusing on concepts integrating the storage and the reactor (usually under evacuated conditions). Only for suspensions or liquid TCM, separate reactor concepts were found, as well as spraying designs.
- Various concepts were proposed for the evaporator design, focusing on providing a large interface area for the evaporation, as well as limiting the variation in the level of the liquid in the evaporator.
- With respect to systems, Climatewell patented a master-slave TCM system, making simultaneous charging and cooling possible.

For the material aspects, both data on a large amount of active materials were presented, as well as aspects related to supporting these materials in a matrix, e.g. based on cellulose. Furthermore, liquids suitable for suspension reactors based on  $\text{NH}_3$  were presented by Rockenfeller.

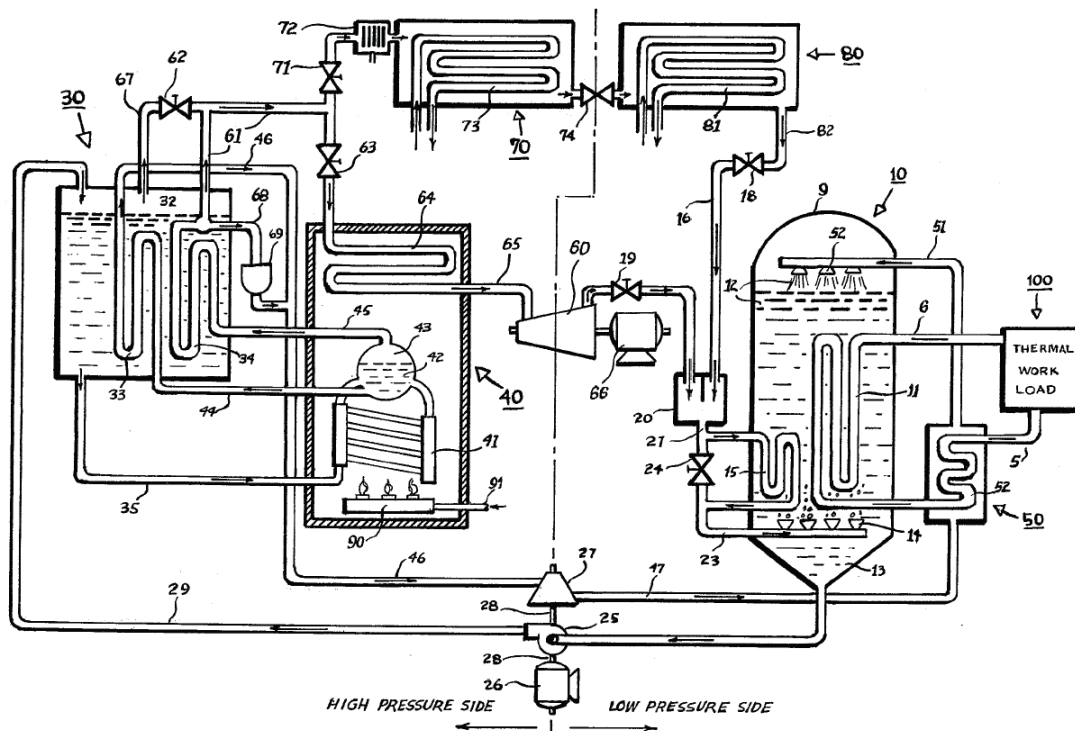
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## **Introduction**

At ECN, long-term research is carried out on the storage of heat by means of thermochemical reactions, in which a vapour is absorbed into a salt or adsorbed into a porous material. To avoid overlap with earlier research, it was decided to make first two inventories of ongoing research on TCM systems, and of patents issued over the years on TCM systems. All together in this report on TCM patents, 18 patents are presented. The patents from TNO and one patent from Rockenfeller take into account suspensions of TCM. In addition, a number of patents from Climatewell / Suncool refer to systems using both solid and liquid hydrates in a three-phase system. Finally, the patents from Brunberg, De Beijer and the later patents from Rockenfeller focus on fixed bed systems. The patents of Rockenfeller describe various means of optimizing the TCM system by optimizing the heat exchanger desing, the beneficial effect of using a matrix to prevent volumetric change of the TCM and the beneficial effect of amine additives to the water. The patents of Climatewell explain the optimization of a TCM chiller concept by adding a slave chiller that can chill while the main system is charging, and also propose an optimized sprayer arm for liquid distribution, the use of surface enlarging means, various configurations for the TCM system and optimized evaporator concepts (also mentioned by De Beijer).

# Patents

## Hartman, 1977, US4009575



[57]

### ABSTRACT

A method, and apparatus for implementing the method, for simultaneously generating electrical power and producing refrigeration, utilizing an absorption/re-generation power cycle, and performing useful work with the heat rejected from the cycle. In the cycle, a working fluid is absorbed by a carrier fluid by an exothermic chemical reaction wherein the heat released is utilized to perform useful work. After absorption, the original fluids are regenerated by an endothermic chemical reaction with the required energy supplied by an external prime source. Surplus energy stored in the fluids after regeneration is extracted and utilized to generate electrical power, produce refrigeration, and provide internally required energy.

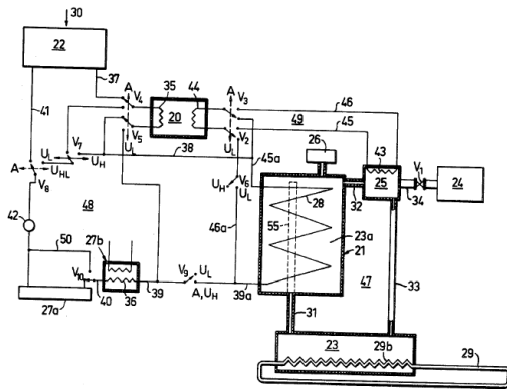
20 A working fluid in gaseous form is injected into the carrier fluid 12 by means of a set of nozzles 14. As described hereinabove, a number of fluid pairs are suitable to carry out the method of our invention. However, we have found that the use of carbon dioxide 25 (CO<sub>2</sub>) as the working fluid and an aqueous solution of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) as the carrier fluid are capable of producing the highest efficiency. Although we are not to be limited to the use of these fluids, the reactions in the cycle will be described in terms of 30 carbon dioxide and potassium carbonate.

The aim of the system is to generate a pressure difference to drive turbine 60. The system is based on the reaction  $K_2CO_3(aq) + H_2O(l) + CO_2(g) \rightarrow 2KHCO_3(s)$ . The CO<sub>2</sub> (32) is evaporated from the carrier liquid K<sub>2</sub>CO<sub>3</sub>(aq) + H<sub>2</sub>O(l) in heat exchanger 30 by means of heat from boiler 40, and is expanded in turbine 60, after which the CO<sub>2</sub> is again absorbed in the liquid in absorber 10. This liquid is subsequently pumped by means of pump 25 to heat exchanger 30. In addition, the system can also provide cooling by cooling the CO<sub>2</sub> to liquid form in 70, with cold from 73, after which the liquid CO<sub>2</sub> is expanded in 80, thereby chilling the fluid in 81. The diluted solution from 30 is returned to absorber 10

through turbine 27 (on the same axis as pump 26 to reduce the pumping energy demand).



## Brunberg, 1980, US4186794



[57]

### ABSTRACT

Heat energy is stored chemically in and extracted from an energy accumulator containing a substance which contains less liquid in the charged, high-energy condition of the accumulator than it does in the discharged low-energy condition of the accumulator, which is associated with vapor condensing and generating means which is maintained at a low temperature as compared with the accumulator in which a liquid container is comprised. Vapor is driven off from the accumulator substance and transferred to the vapor condensing and generating means when energy is stored in the accumulator, and is returned to the accumulator when heat energy is extracted therefrom. The system comprising the accumulator and said vapor condensing and generating means is maintained substantially free from other gases than said vapor.

By means of a solar collector system (22) an accumulator (21) is charged, and the vapour is condensed in the condenser 25, which may be drained to the water tank 23. The system consisting of the condenser and accumulator is at low pressure, controlled by the vacuum pump 26 and the manometer 25. At discharging, the  $\text{Na}_2\text{S}$  (or  $\text{CaCl}_2$ ) in the accumulator is hydrated, and the output heat is backed up by the heat pump 20, providing heat to the space heating system 27a and the DHW system 27b.

Solar collector 22 for converting solar and sky radiation 30 to heat energy to be supplied to the accumulator 21 at charging. The transport medium is a liquid, but preferably not water, if the liquid is passed through the piping 28 of the accumulator 21. (A water leakage in the accumulator would result in rapid energy development and pressure increase in the accumulator when a salt rich in energy is used).

It is emphasized that the system should be evacuated.

The vapor pressure in the system should substantially be constituted by water vapor. If other gases were present, for example air, this would render the flow or the water vapor between the containers  $B_2$  and  $B_1$  more difficult. An increase in the partial pressure due to other gases would rapidly slow down the speed of the process.

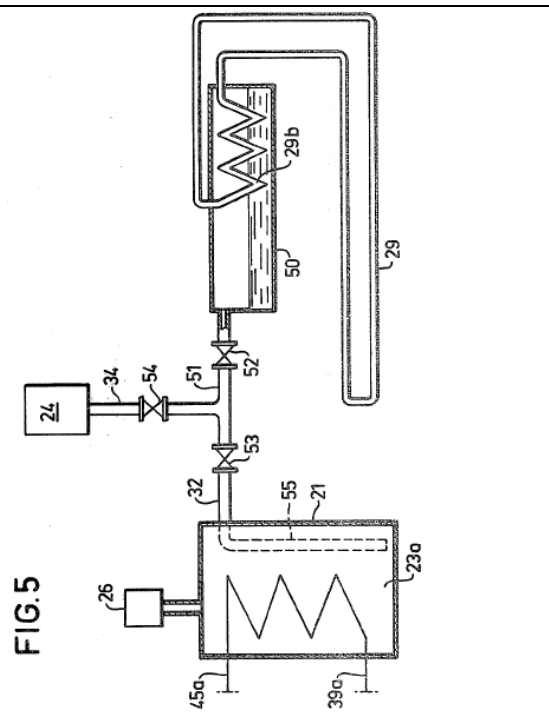
Vacuum pump 24 for a pressure limit of about 0.5 torr. The pump is connected to the accumulator 21 via a conduit 34 with a valve  $V_1$  and a condenser 25.

Pressure-sensing member or manometer 26, which electronically starts the vacuum pump 24 and opens the valve  $V_1$  if the partial pressure of gases other than water vapor in the accumulator 21 exceeds a predetermined value (some torrs).

However, it would be possible to store the water under non-vacuum conditions:

It has been presumed above that the system has been designed as a closed system, which, however, is not absolutely necessary. At the drying process it may be practical when applying the method to successively remove the water amount (several m<sup>3</sup>) condensed during the process in the container B<sub>2</sub>. At the extraction of energy it is then necessary to supply water from outside to the system. The water removal and supply in question is carried out so that foreign gases are not simultaneously introduced into the system or, if such introduc-

At charging the level sensor is activated when the water level in the container 50 has risen to a predetermined maximum value. Then valve 52 is shut and the valves 57 and 59 are opened. Water is evacuated to a sink through valve 57 and the conduit 58 simultaneously as air of atmospheric pressure is supplied to the container 50 through valve 59 and conduit 60. When the container 50 has been drained, valves 57, 59 and 53 are closed. After that pump 24 is started and valves 54 and 52 are opened, air in the container 50 then being evacuated during a suitable pumping time. After that valve 54 is closed, pump 24 is stopped and valve 53 is opened.

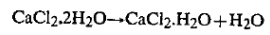


As a modification, it is claimed that several systems could be put in series to produce heat of 150-200 C, to be used to produce electricity in a Carnot cycle.

The patent also provides detailed information on the drying on CaCl<sub>2</sub>

20 The regeneration or drying of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  in the  
 container  $B_2$  takes place at energy storage. The process  
 then runs in a direction opposite to that at energy ex-  
 traction. Heat energy ( $Q_1$ ) is supplied to the container  
 25  $B_1$ , which is given a temperature of, for example,  $+100^\circ$   
 C. while the container  $B_2$  is held at a low temperature,  
 for example  $+5^\circ$  C. to  $+10^\circ$  C. The water vapor pres-  
 sure in  $B_2$  then is about 10 torr. The solution of  
 30  $\text{CaCl}_2 + 6\text{H}_2\text{O}$  found at the beginning of the drying in  
 the container  $B_1$  has a high vapor pressure and boils,  
 whereby water is released and collected in  $B_2$ .

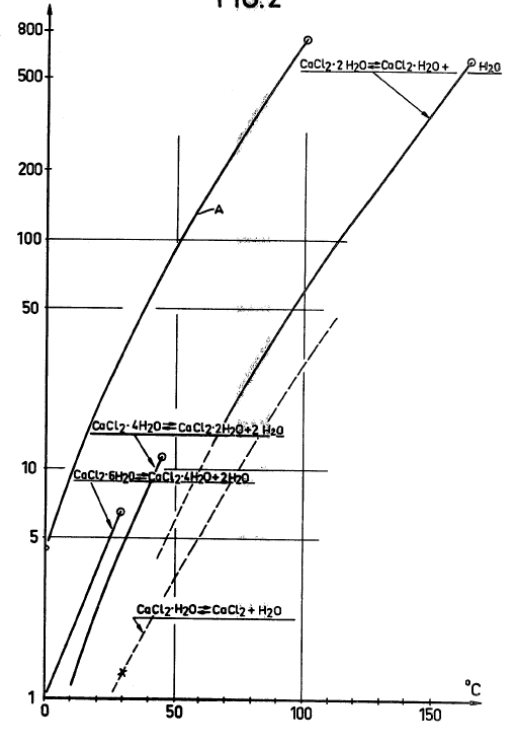
35 The drying of salt ( $\text{CaCl}_2$ ), however, according to the  
 method described above is difficult to carry out in a  
 simple way in practice. The drying process proceeds  
 very slowly at the equilibrium transition



40 The reason for this is that  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  forms needle-  
 shaped crystals in liquid  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  whereby the gas  
 passage successively becomes more difficult and finally  
 is restricted to a few channels where complete drying of  
 the salt to  $\text{CaCl}_2$  occurs within limited areas.

45 A closed system permits the use of salts, which are  
 unstable at their boiling point under atmospheric pres-  
 sure, but can be dried at a lower temperature and pres-  
 sure.  $\text{Na}_2\text{S}$ , for example, can suitably be used.  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$   
 has been dried with good result according to the  
 low-pressure method at  $+100^\circ$  C.  $\text{Na}_2\text{S}$  and its hydrates  
 remain in crystalline form during the whole process.

FIG. 2

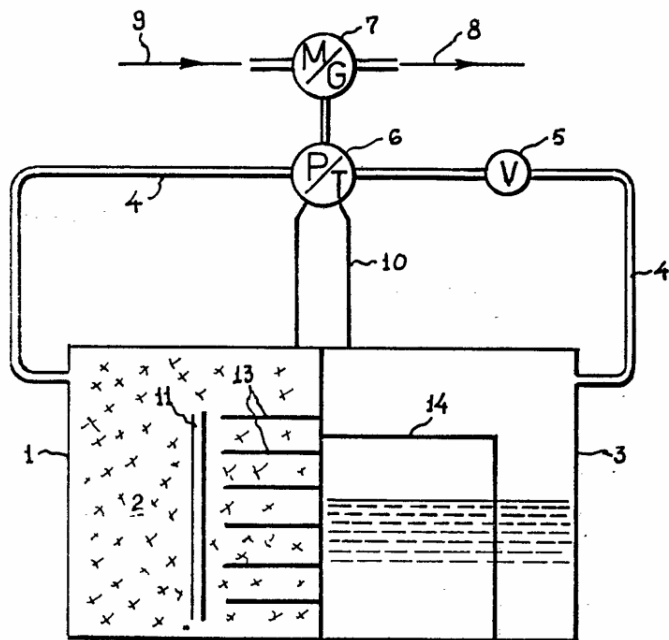


## Brunberg, 1981, WO81/01726

(54) Title: METHOD OF STORING ENERGY AND SYSTEM FOR CARRYING OUT THIS METHOD

### (57) Abstract

In a method of storing energy in a two-vessel system, in which one vessel (1) contains a first substance (2) comprising two components, one of which is driven off from and is caused to become absorbed by the other component, respectively, at the supply of energy to and the withdrawal of energy from the system, respectively, energy is stored in the system by pumping said one component out of said one vessel (1). A system for carrying out this method comprises a two-vessel system, in which one chamber (1) contains a first substance (2) which comprises two components, one of which may be driven off from the other component, which on its side has the capability of absorbing said one component. The system also comprises an energy converter (6) adapted for the sucking or pumping out of said one component and which is incorporated in a conduit (4) connected to said one chamber (1). Thanks to the above method and system it has become possible to store mechanical or kinetic energy, e.g. from a wind power plant, in the form of chemical energy for later removal of mechanical or kinetic energy without the necessity of passing through heat energy.

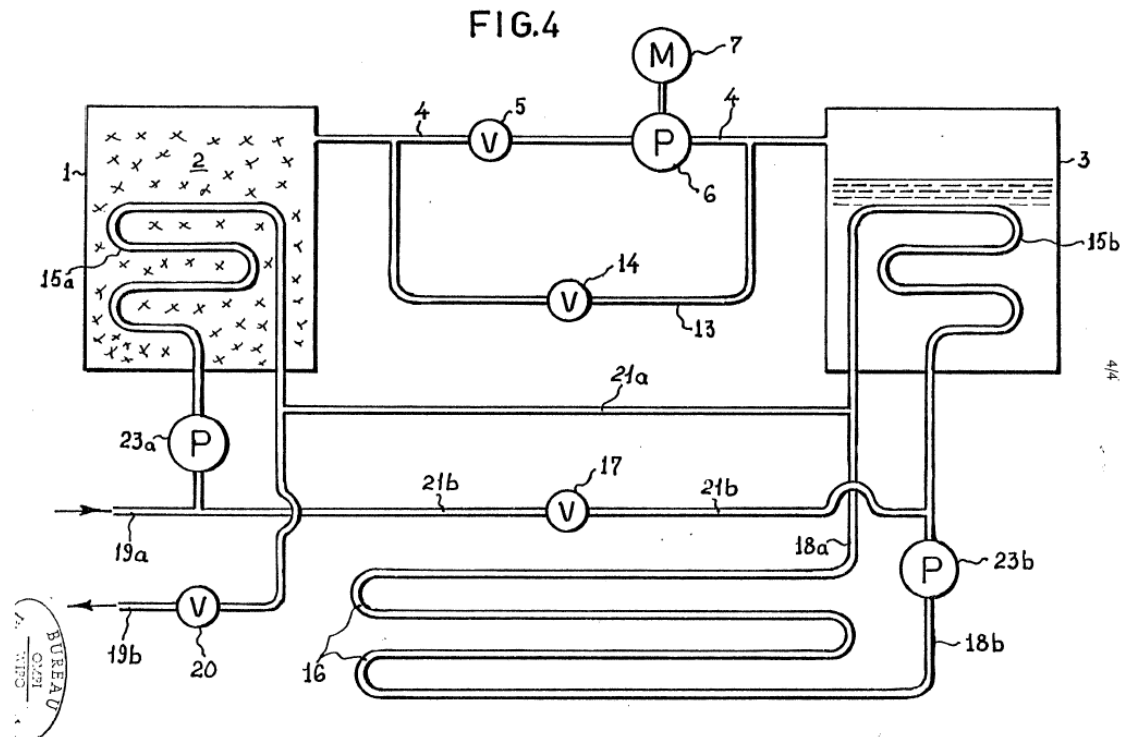


The patent focuses on  $\text{Na}_2\text{S}$ . The patent describes the basic means to increase vapour and heat transfer.

15 In Fig. 1 1 designates said one chamber or vessel which contains a salt  $\text{Na}_2\text{S} \cdot n\text{H}_2\text{O}$  as said one substance 2. 3 is the other chamber or vessel of the system, which contains water and is in thermal equilibrium with the chamber 1 (and accordingly is thermally connected to and has substantially the same temperature as the chamber 1). The 20 chambers 1 and 3 communicate with each other through a tubular conduit 4 which comprises at least one valve 5 and in which an energy converter 6 is interconnected. In the substance 2 there is provided one or more gas channels 11 25 to facilitate the gas transport to and from the substance, as well as a set of metal flanges 13 in contact with the wall 12 to facilitate or enhance the distribution of the heat energy between wall and salt mass. In the chamber 3 there are also provided a plurality of suitably vertical 30 and mutually parallel metal fins or the like 14 to provide a good thermal contact between the wall 12, the liquid in the chamber and pumped-in, condensable gases. Said flanges or fins are suitably provided with a liquid absorbing material, e.g. fabric at least partially, to facilitate the distribution of the liquid over a larger area when the liquid is vaporized at the discharge of the system and heat energy is consequently transferred from the fins to the vaporized liquid.

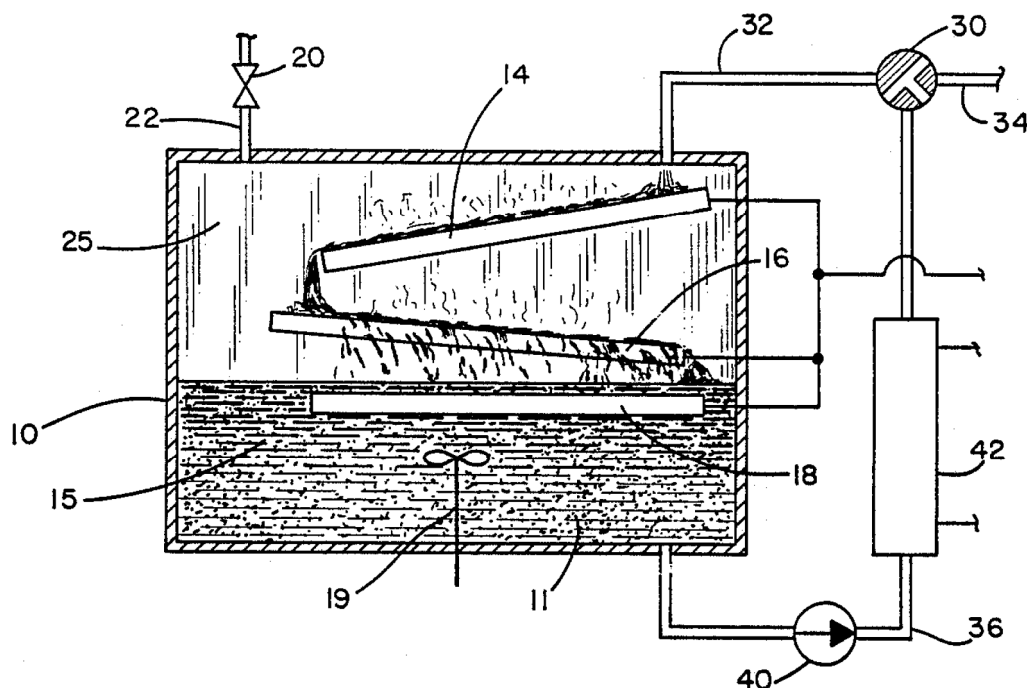
In the form shown above, the heat released on hydration is partially conducted through the wall to the water, assisting in the vaporization of the water (which lowers the storage density). The idea is to use a fan driven by wind energy to charge the system up to a pressure difference of up to 0.5 bar, and to discharge the system by driving a turbine located at point 6, thereby making this system a means to store mechanical energy.

As an alternative, however, it is also indicated that the system could function as a means to store heat (see figure 4). The vessels are now separate and the water is evaporised by means of energy from a borehole or a heat exchanger (16) at the bottom of a lake.



## Rockefeller, 1989, US 4822391

Uwe Rockefeller has over 60 patents over the period 1989-2005, almost all in the field of absorption heat pumps. Only a very limited selection can be presented here.



[57]

### ABSTRACT

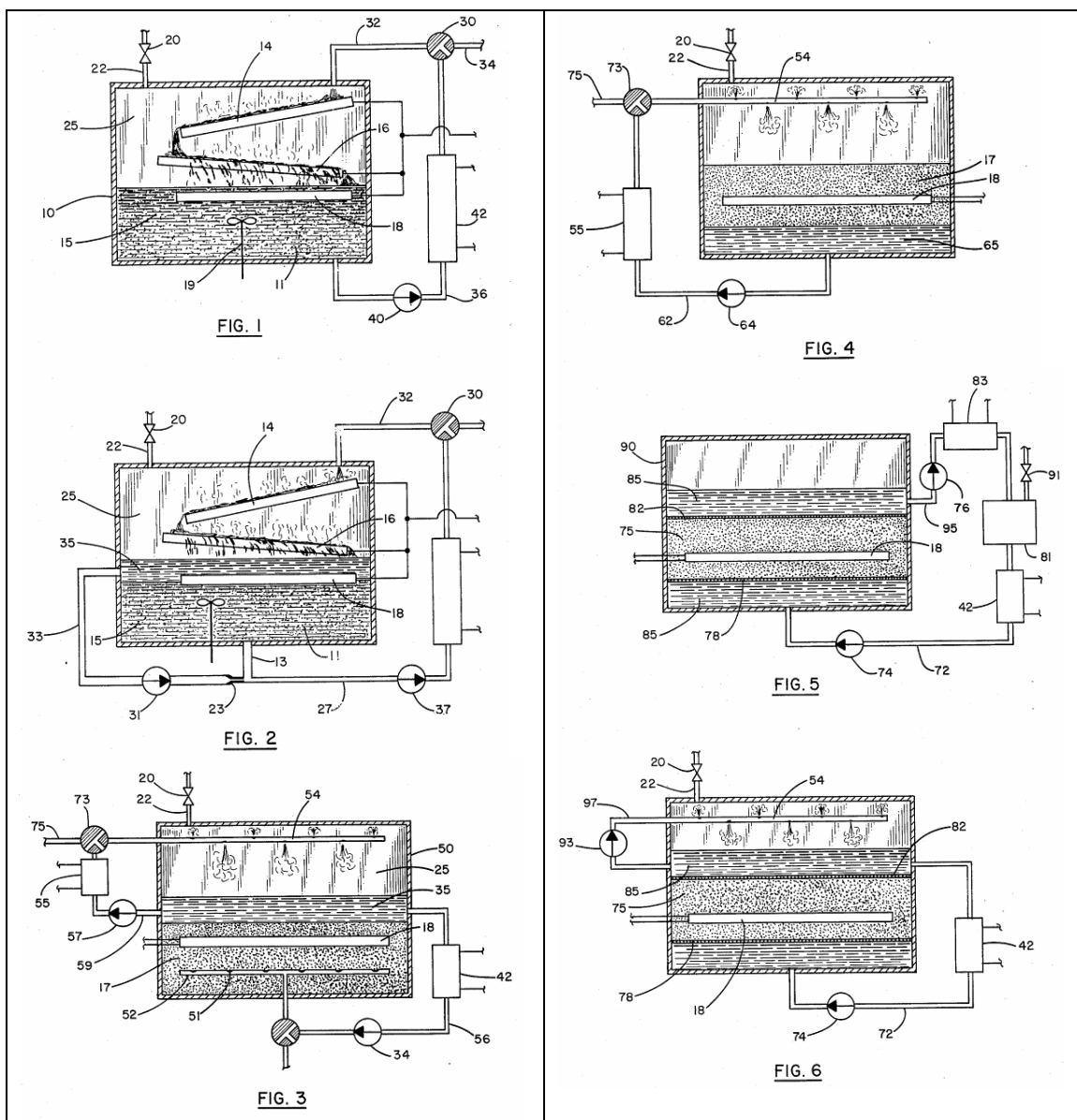
Energy and mass are transferred in a system utilizing a gaseous refrigerant which is mixed and sorbed (absorbed/adsorbed) with a liquid carrier selected from the group consisting of long chain alcohols, ethers, glycols, glycol ethers, sebecates, phthalates, aldehydes and ketones, and sorbate/liquid mixture then combined with a particulate solid capable of forming a solid/gas compound with the gaseous refrigerant. The process is carried out in a mass and heat exchange apparatus capable of collecting and transferring the energy created by the formation or dissociation of the solid/gas compound.

In carrying out the process of the invention, depending on the nature of the individual gaseous, liquid, and particulate solid components of the system, it may be advantageous to first form a mixture or slurry of the liquid and particulate solid and then introduce the gaseous refrigerant which first complexes with the liquid carrier which liquid mixture is then mixed with the solid at which time the adsorption reaction will occur. In yet other cases, it may be preferred to first mix the liquid with the gas to form the liquid complex in a separate vessel, which liquid mixture is then introduced into the energy and mass transfer apparatus for carrying out the adsorption process.

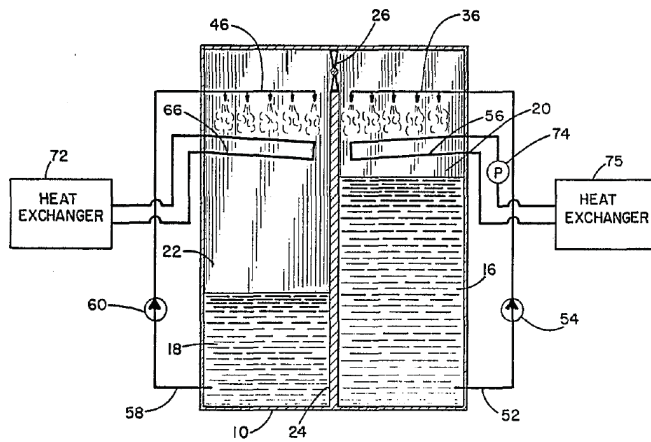
The liquid must also remain in the liquid state during adsorption and desorption conditions of the process. Moreover, the liquid is to keep the solid in a pumpable suspension or it must separate from the solid after the sorbate (adsorbate/absorbate) exchange.

Suitable liquids meeting the aforesaid condition may be selected from the following group and include long chain alcohols, preferably aliphatic carbon chains having at least seven carbon atoms and the isomers thereof, ethers, glycols, glycol ethers, sebecates, phthalates, aldehydes and ketones, again preferably those having alkyl chains of at least seven carbon atoms. Specific examples of suitable liquids include octanol, diethylene glycol, diethylene glycol diethyl ether, diethyl sebecate, diethyl phthalate and succinaldehyde. Such liquids are by the way of example only and are not intended to be limiting.

The patent gives a system in which a liquid is used for the transport of the gas flow and/or the particle flow. The gas is fed to the reactor through valve 20 and various means are indicated in which the gas can be transferred to the liquid. Various embodiments are presented, such as a gravitational system (figure 1, with additional a system in figure 2 in which the liquid is lighter than the slurry), a spraying system (figure 3, in which the liquid is lighter or figure 4, in which the liquid is heavier), and finally two systems in which the active material is enclosed between two porous plates that allow passage of the liquid but not of the solid, in which the liquid is either sprayed in the gas-filled reactor (figure 6) or loaded with the gas flow in an external device 91 (figure 5).



**Rockefeller, 1989, US 4823864**



[57]

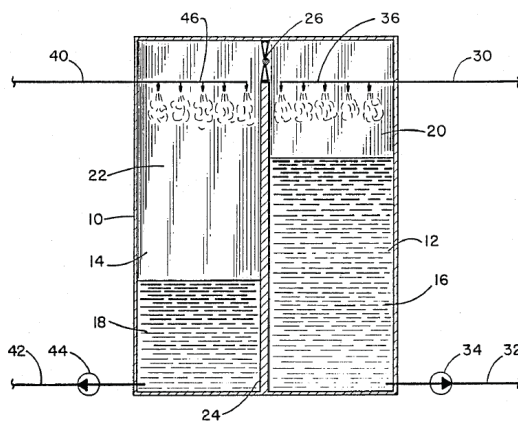
**ABSTRACT**

A system for storing chemical energy comprises first and second vessels, the first containing a liquid solution of an alkali or alkaline earth metal hydroxide, halide, or thiocyanate, or ammonium halide or thiocyanate at an initial concentration of between about 30% to about 80%, by weight, the second vessel containing liquid, a space about the liquid in each vessel and a conduit communicating between the spaces having a valve for selectively allowing liquid vapor to pass between the spaces, means for heating the solution to a temperature above about 80° F., means for cooling the liquid to a temperature below about 55° F., and heat exchange means for transferring heat from the heated solution and for transferring heat to the cooled liquid. Water is the preferred liquid although ammonia, lower alcohols, and polyols such as glycerol, glycols, polyglycols, glycol ethers, lower aliphatic amines and alkanol amines, and mixtures thereof, may be used.

During this discharge cycle, valve 26 must be opened 10 and because of the difference in vapor pressure between the first and second spaces, 20 and 22 respectively, water is evaporated in second space 22 to provide substantial cooling of the liquid in second vessel 14. At the same time, the evaporated water is passed into first 15 space 20 where it is absorbed into solution 16, which causes a heat of condensation and solutions in first vessel 12, which heat is again exchanged by the outside cooling means (not shown) previously discussed. Alternatively, the heat of condensation and solutions in first 20 vessel 12 may be used for heating purposes, for example in a dual temperature storage capability for building heating and cooling.

Liquid (18) is preferentially water and the active solution (16) can be an aqueous solution of a suitable hydroxide, chloride, bromide or nitrate. As an alternative, ammonia could be used for the liquid (18), in which case (16) could be an ammonium salt solution; various salts are mentioned among which  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$ .

As an alternative embodiment, the heat exchange can also be done directly from circuit 58 and circuit 52, instead of with heat exchangers 72 and 75, resulting in the system below.



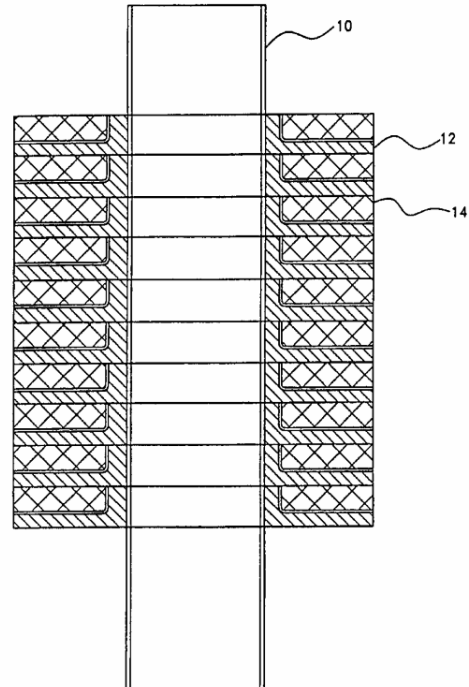


## Rockefeller, Rocky research, 2000, WO 00/66954

(54) Title: IMPROVED HEAT AND MASS TRANSFER APPARATUS AND METHOD FOR SOLID-VAPOR SORPTION SYSTEMS

### (57) Abstract

A sorber heat exchanger is provided with a substrate material incorporating a sorbent for reacting with a polar gas refrigerant or hydrogen. A preferred sorbent is a metal salt capable of reacting with the polar gas refrigerant to form a complex compound. The sorbent incorporating substrate is loaded into the reactor space between the heat transfer surfaces. Incorporating the sorbent into the substrate reduces sorbent migration thereby improving performance and life expectancy of the heat exchanger.



The patent focuses on the use of fibrous materials for incorporating the salt (14), such as an ammonia salt (that show a large expansion on ammoniakation), thereby improving the reliability of the system. The impregnated fibrous material can e.g. be incorporated in a finned structure (12).

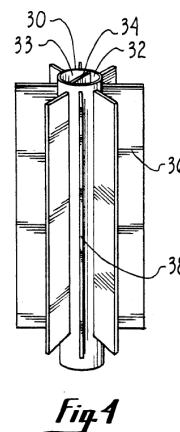
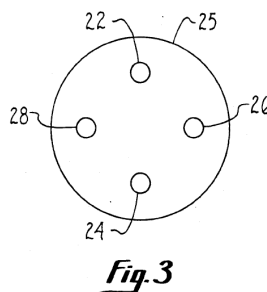
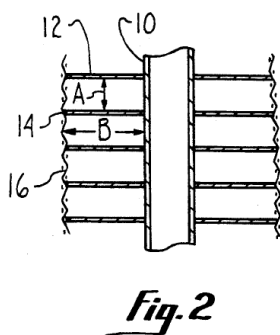
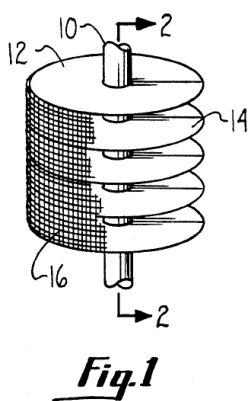
According to the present invention solid sorbent migration in a reactor in which solid vapor sorption is carried out is substantially reduced or eliminated by incorporating the sorbent on a suitable substrate material. The solid  
30 sorbent used in the improved reactors and systems of the invention are metal salts, or complex compounds produced from the salts, or metal hydrides. The substrate material incorporating the metal salt, complex compound or metal hydride may be a woven material such as a fabric or cloth, an unwoven material such as yarn, felt, rope, mat or similar material in which the strands or fibers have been tangled or otherwise mixed, twisted, pressed or packed to form a coherent substrate. Woven fabric layers may be used between unwoven layers of fibers, especially in composites of

alternating woven and unwoven fiber layers. Yarn, rope, or strips or ribbons of substrate fabric may also be used for certain reactor heat exchanger designs.

Specific preferred substrate materials include nylon polymers including non-aromatic nylons or polyamids, aromatic polyamides or aramids, fiberglass, and polyphenylene sulfides. The aramids are preferred for complex compounds operating at reaction temperatures below about 150°C. For higher temperatures, fiberglass and polyphenylene sulfides are preferred, while at temperatures below about 120°C, nylon-based polymer materials are also suitable. Aramids are not recommended at reaction temperatures above about 150°C. Substrate materials having a high thermal conductivity are advantageous since they improve heat transfer properties of the heat exchanger sorber core. The thermal conductivity of aforesaid substrate materials may be enhanced by incorporating highly thermal-conductive materials such as fibers, particulates, etc. into the substrate.

To obtain high thermodynamic and mass efficiency of the substrate composition, it is desirable to use a physical form of the material which can be loaded with a high mass fraction of the sorbent. It is preferable that at least 50%, and preferably 70%, and most preferably 85% or more, of the volume of the sorbent/substrate composition comprises the sorbent itself. Thus, a preferred substrate material used to produce the sorbent/substrate composition of the invention has a porosity of about 50% or more and up to about 98%. Examples of types of fabric used to meet such open volume and porosity requirements include textile materials such as cloth, fabric, felt, mat, etc., commonly formed by weaving or knitting, as well as non-woven but cohesive forms such as batt or batting and the like. Woven structures have the advantage of greater strength, although the use of reinforcement layers integrated into any substrate material may be desirable to further increase the strength of the substrate. Where reinforcement layers are used, it is important to control substrate separation at the reinforcement interface. It has been found advantageous to use a substrate material sufficiently gas permeable for the refrigerant gas to pass through and sufficiently low in pore size to prevent small salt particles to penetrate. Although woven materials usually provide superior physical and structural uniformity, the use of non-woven or amorphous fiber substrates may provide for more uniform distribution of solid sorbent throughout the pores, spaces and interstices of the material.

### Rockefeller, Rocky research, 1994, US5328671



According to the present invention, the reaction rates of adsorption and desorption of a polar gas with a complex compound consisting of the polar gas and a metal salt are increased by carrying out at least the initial adsorption reaction under conditions so as to achieve a complex compound having a physical structure different from the unreacted salt, and which is at least partially a physically coherent, cohesive, self supporting mass. Such a reaction product is achieved by optimizing the density of the complex compound by limiting the volumetric expansion of the complex compound formed during the initial adsorption reaction. The complex compounds have a potential reaction product volume increase of between about 10% and up to about 1000% of the volume of the original uncompact and unreacted salt. This growth occurs substantially during the initial adsorption of the polar gas on the previously unreacted metal salt. Where the initial adsorption reaction is allowed to proceed without controlling the reaction product density by restricting the volumetric expansion, the resulting reaction product does not achieve the desired coherent, self-supporting mass. Instead, the product is amorphous and powdery, and the product mass will not support its shape or structure. Moreover, once the complex compound is so formed, the physical characteristic of the product is substantially irreversible, and the desired structure cannot be achieved by further adsorption or desorption unless the complex compound is desorbed, and thereafter introduced into a volumetrically restricted heat exchanger (reaction chamber) cavity and reacted according to the invention. It is also found that such a volumetrically unrestricted complex compound reaction product has substantially reduced adsorption/desorption reaction rates as compared to reaction products in which the volumetric expansion is limited and the density of the reaction product is controlled.

It may also be advantageous to utilize a mixture of the two or more aforesaid metal salts, for example, one salt which yields a relatively high volumetric expansion complex compound and another salt which has a lower volumetric complex compound expansion. By using a mixture or combination of such salts, for example strontium chloride with calcium chloride or magnesium chloride, or calcium bromide with calcium chloride, the resulting structure may have reaction rates improved from either of the salts, when used alone.

#### Fin count

Adsorption rate tests were run for  $\text{CaBr}_2 \cdot 2-6 \text{NH}_3$  with the salt held at  $108^\circ \text{C}$ . and ammonia pressure of 3.93 bars applied. The heat exchanger had a fin height of 0.7 inches and salt was loaded at 0.7 grams of unammoniated salt per cubic centimeter of salt holding volume on the heat exchanger. For fin counts of 7, 12, and 14 fins/inch, the following results were obtained:

Fin count	k
7	0.068
12	0.142
14	0.118

Fin counts of 12 give the maximum sorption rates at these temperature and pressure conditions, with other heat exchanger parameters being equal.

#### Fin height

Adsorption rate tests were run for  $\text{CaBr}_2 \cdot 2-6 \text{NH}_3$  with the salt held at  $35^\circ \text{C}$ . and ammonia pressure of 0.272 bar ( $-70^\circ \text{F}$ . evaporator temperature) applied. The heat exchangers all had a fin count of 5 fins/inch and salt was located at a density of 0.6 grams of unammoniated salt per cc. Fin heights of 0.35", 0.375", and 0.40" were tested.

Fin height	k
0.350	0.073
0.375	0.081
0.400	0.059

At these temperature and pressure conditions, a fin height of 0.375 gives the optimum reaction rate, although minimum system cost (cost per unit of cooling capacity obtained at  $-70^\circ \text{F}$ .) is obtained with a fin height of 0.40 inches due to reduced heat exchanger and vessel costs.

#### Salt loading density

Adsorption rate tests were run for  $\text{CaBr}_2 \cdot 2-6 \text{NH}_3$  at 3.93 bar with the salt at  $108^\circ \text{C}$ . All heat exchangers had a fin count of 7 fins/inch and a fin height of 0.40. Loading densities of 0.5, 0.6, and 0.7 grams salt/cubic centimeter salt holding volume on the heat exchanger were run:

Loading density	k
0.5	0.087
0.6	0.132
0.7	0.075

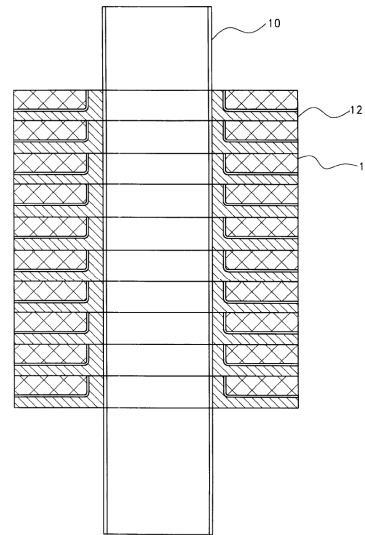
Maximum rates (maximum k) are obtained with a loading density of 0.6 g/cc. Minimum system cost is obtained with a loading density of 0.7 because more salt is contained in a given amount of heat exchanger and vessel volume.

The reactivity of the salts may be further enhanced by initially adsorbing a small amount of a gaseous ligand on the salt, which additive ligand is different from the gaseous reactant to be used in the complex compound. Any of the aforesaid polar gaseous reactants may be used, and particularly preferred are water, ammonia, lower aliphatic alcohol, amines, or phosphine. The amount of the additive material is preferably between about 0.05% and about 10% by weight of the salt. The use of a hydrated salt containing a small but effective amount of water adsorbed on the salt may be satisfactory for such a purpose.

**Rockefeller, Rocky research, 2001, US6224842**

**SUMMARY OF THE INVENTION**

In the present invention, a sorber heat exchanger, i.e., a reactor, is provided with a sorbent/substrate composition comprising a substrate material substantially inert to a polar gas and incorporating a salt of a metal on which the polar gas is to be absorbed or with a complex compound formed by absorbing the polar gas on the metal salt. The use of the sorbent/substrate composition results in substantial micro-immobilization of the solid sorbent. According to the invention, it has been found that for sorption processes in which repetitive absorption and/or desorption reactions in excess of 200 repetitions exceed, at least temporarily, reaction rates of 3 moles gas/mole sorbent-hr, sorbent migration is substantially reduced by utilizing a suitable substrate material on or in which complex compounds or metal salts have been incorporated. Reduced sorbent migration improves the performance of the apparatus as well as the sorption cycle capability and expected life of the apparatus. The aforesaid invention is also useful in metal hydride sorption systems in which hydrogen is alternately absorbed or desorbed, particularly if high reaction rates or multiple thousand reaction cycles are desired. Such improvements as well as a more detailed description of the invention are described hereinafter.



**FIG. 7**

50 According to the present invention solid sorbent migration in a reactor in which solid vapor sorption is carried out is substantially reduced or eliminated by incorporating the sorbent on a suitable substrate material. The solid sorbent used in the improved reactors and systems of the invention are metal salts, or complex compounds produced from the salts, or metal hydrides. The substrate material incorporating the metal salt, complex compound or metal hydride may be a woven material such as a fabric or cloth, an unwoven material such as yarn, felt, rope, mat or similar material in which the strands or fibers have been tangled or otherwise mixed, twisted, pressed or packed to form a coherent substrate. Woven fabric layers may be used between unwoven layers of fibers, especially in composites of alternating woven and unwoven fiber layers. Yam, rope, or strips or ribbons of substrate fabric may also be used for certain reactor heat exchanger designs.

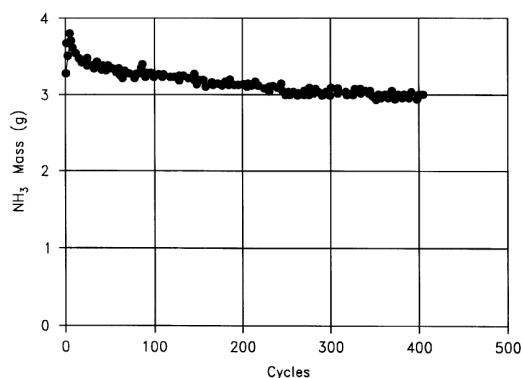
60 Specific preferred substrate materials include nylon polymers including non-aromatic nylons or polyamids, aromatic polyamides or aramids, fiberglass, and polyphenylene sulfides. The aramids are preferred for complex compounds operating at reaction temperatures below about 150° C. For higher temperatures, fiberglass and polyphenylene sulfides are preferred, while at temperatures below about 120° C., nylon-based polymer materials are also suitable. Aramids are not recommended at reaction temperatures above about 150° C. Substrate materials having a high thermal conductivity are advantageous since they improve heat transfer properties of the heat exchanger sorber core. The thermal conductivity of aforesaid substrate materials may be enhanced by incorporating highly thermal-conductive materials such as fibers, particulates, etc. into the substrate.

To obtain high thermodynamic and mass efficiency of the substrate composition, it is desirable to use a physical form of the material which can be loaded with a high mass fraction of the sorbent. It is preferable that at least 50%, and preferably 70%, and most preferably 85% or more, of the volume of the sorbent/substrate composition comprises the sorbent itself. Thus, a preferred substrate material used to produce the sorbent/substrate composition of the invention has a porosity of about 50% or more and up to about 98%.

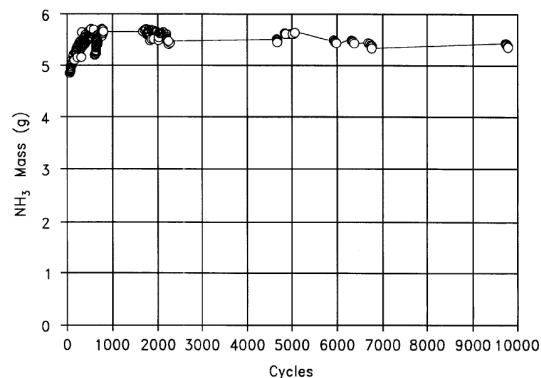
Examples of types of fabric used to meet such open volume and porosity requirements include textile materials such as cloth, fabric, felt, mat, etc., commonly formed by weaving or knitting, as well as non-woven but cohesive forms such as batt or batting and the like. Woven structures have the advantage of greater strength, although the use of reinforcement layers integrated into any substrate material may be desirable to further increase the strength of the substrate. Where reinforcement layers are used, it is important to control substrate separation at the reinforcement interface. It has been found advantageous to use a substrate material sufficiently gas permeable for the refrigerant gas to pass through and sufficiently low in pore size to prevent small salt particles to penetrate. Although woven materials usually provide superior physical and structural uniformity, the use of non-woven or amorphous fiber substrates may provide for more uniform distribution of solid sorbent throughout the pores, spaces and interstices of the material.

The sorbent is incorporated in the substrate material by embedding or impregnating or otherwise combining the two components to form the sorbent/substrate composition to be installed in a sorber heat exchanger according to the invention. The preferred method of incorporating the sorbent into the substrate material is by impregnation. Such impregnation is carried out by any suitable means such as spraying the substrate material with a liquid solution, slurry, suspension or mixture containing the sorbent or soaking the substrate in a liquid solution, slurry or suspension of the sorbent followed by removal of the solvent or carrier by drying or heating, and/or by applying a vacuum. The slurry or suspension may also be used or mixed with a sorbent compatible binder for stabilizing and further reducing migration of the sorbent in or within the substrate. The substrate may also be impregnated by pumping the salt suspension, slurry or solution or liquid-salt mixture into and through the material, whereby the substrate also functions to filter the impregnating compositions. Yet, other methods for incorporating sorbent into the substrate include embedding or otherwise distributing fine sorbent particles within the substrate using blowing, blasting or sintering methods and techniques.

CaBr<sub>2</sub> without substrate



CaBr<sub>2</sub> with substrate



## ***Chandler and Rockefeller, Rocky research, 1998, US5829259***

[57]

### **ABSTRACT**

The rate of water vapor sorption of an absorption cycle cooling and/or heating system using an aqueous alkali metal halide or hydroxide solution as the working fluid is increased by adding to the fluid an effective additive amount of at least 2 parts per million of a primary, secondary or tertiary aliphatic, cycloaliphatic, heterocyclic or aromatic amine to the fluid capable of increasing the rate of water vapor absorption.

### **81 Claims, No Drawings**

5 According to the invention, it has been found that the presence of an amine in the aqueous absorption fluid containing a lithium halide or the sodium or potassium hydroxides, or mixtures of the hydroxides results in substantially improved heat and mass transfer performance of the absorption working fluid composition. Specifically, the performance of the system improves in the following manner: water cooling temperature change in the absorber, for a constant water flow rate, rises significantly; the absorber power load increases proportional to the change in water cooling temperature; the steady state vapor pressure drops, and if brought back to its initial value to achieve a constant evaporator temperature, the change in concentration of the absorber fluid increases significantly; the absorber solution subcooling, i.e., the difference between the maximum temperature at equilibrium (saturation) and the actual solution temperature, is decreased by several degrees; the absorber solution-heat exchanger tube interface comprises a highly agitated turbulent film as compared to a generally laminar flow pattern without presence of the additive; and overall heat transfer coefficients and sorption fluid film heat transfer coefficients are increased.

45 For the alkali metal halides, and particularly the lithium bromide solutions, the most preferred amines are ethylhexylamine, N,N-dimethyloctylamine, aniline and benzylamine. Other examples of useful aliphatic amines include tert-octylamine, n-octylamine, di-sec-butylamine, pentylamine, butylmethylamine, dipropylamine, butylethylamine, triethylamine, pentylethylamine, hexylamine, cyclohexylamine, trans-1,2-diaminocyclohexane, N,N-diethylcyclohexylamine, 1,5-dimethylhexylamine, N,N-dimethylhexylamine, N-methyldibutylamine, nonylamine, N,N-diisopropylethylamine and 2-methyl-1,5-diaminopentane and others disclosed in the aforesaid application and incorporated herein by reference. A most preferred amine additive for the lithium bromide absorption solutions of the invention is 2-ethylhexylamine. Other preferred primary amines include cycloaliphatic or alicyclic amines such as cyclohexylamine and diaminocyclohexane and its different isomers. Other particularly useful and effective amines include secondary aliphatic and saturated cyclic or heterocyclic amines of 4–12 carbon atoms such as dialkylamines, piperidine and substituted piperidines, and pyrrolidine and substituted pyrrolidines. Preferred derivatives are alkyl or halogen substituted. Another preferred group of amines include tertiary aliphatic and saturated heterocyclic amines

## ***Chandler and Rockefeller, Rocky research, 2003, US6656381***

(57)

### **ABSTRACT**

The rate of water vapor sorption of an absorption cycle cooling and/or heating system using an aqueous alkali metal halide solution as the working fluid is increased by adding to the fluid an effective additive amount of at least 2 parts per million of an aliphatic, cycloaliphatic, or aromatic ketone or aldehyde capable of increasing the rate of water vapor absorption.

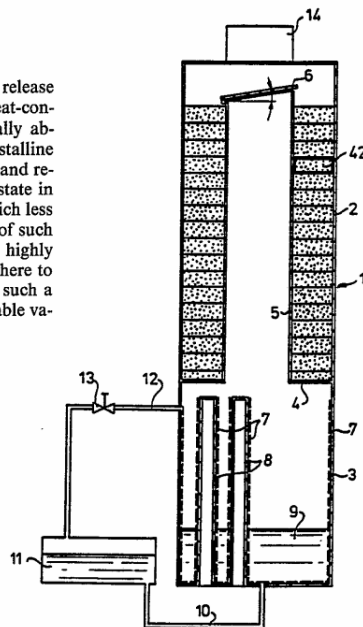
### **32 Claims, No Drawings**

**DeBeijer, DeBeijer Raadgevend Technisch Bureau, 1991,  
WO91/19154**

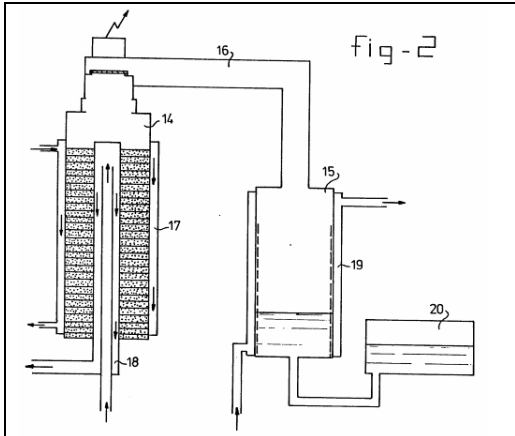
**(54) Title:** HEAT ACCUMULATOR, METHOD FOR THE PRODUCTION THEREOF AND ENERGY SYSTEM PROVIDED WITH SUCH A HEAT ACCUMULATOR

**(57) Abstract**

The invention provides a heat accumulator for the storage and/or release of heat, consisting of a vessel having a wall which is at least partially heat-conducting, which vessel contains a crystalline material which exothermally absorbs and endothermally desorbs a heat-transporting substance. The crystalline material, in particular sodium sulphide, adheres to the wall of the vessel and remains adhering during use and has essentially the same structure in a state in which more heat-transporting substance is absorbed and in a state in which less heat-transporting substance is absorbed. In a process for the production of such a heat accumulator, the crystalline material is applied in the molten or highly hydrated state to the inner wall of a closeable vessel and is made to adhere to the wall by cooling and/or evaporation. An energy system, comprising such a heat accumulator, and a vapouriser and condenser, connected via a closeable vapour line to the heat accumulator, is also provided.



The patent focuses on the method in which the  $\text{Na}_2\text{S}$  layer is fixed to the wall, so as to ensure maximum heat exchange (as an improvement over a loosely poured amount), which is done by inserting a temporary filler body, applying molten or highly hydrated material in the space between the wall and the filler body and subsequently drying it. It was found that for  $\text{Na}_2\text{S}$  this gave a stable structure, while the porosity of the layer could be increased by a slower crystallisation rate. Note that walls 4 and 5 are closed, so that the vapour can only reach the  $\text{Na}_2\text{S}$  through valve 6 (to be opened by magnet 14, not to compromise the gastight housing). The wall 2 has a surface enlarging heat conducting structure (e.g. fins and possibly also graphite). The evaporator below has several capillary gauges 7 to facilitate the vaporization. A reservoir with a large vertical cross section 11 (e.g. a large tube) is used to limit the changes in liquid level in the evaporator.



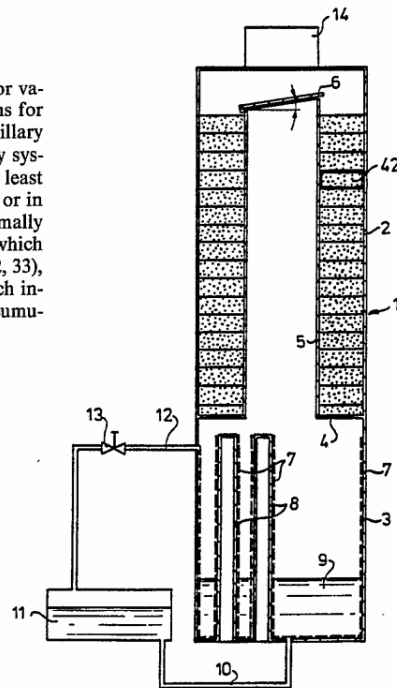
As an alternative (see fig 2), the evaporator (cold section) and accumulator (hot section) can be separated further, to improve the performance (at the cost of a less compact system). In fig 2, also a larger heat exchange area is provided (both 17 and 18).

**DeBeijer, DeBeijer Raadgevend Technisch Bureau, 1991, WO91/19155**

(54) Title: VAPORISER/CONDENSER INSTALLATION AND ENERGY SYSTEM PROVIDED WITH SUCH AN INSTALLATION

(57) Abstract

An installation for the vaporisation or condensation of a liquid or vapour respectively, is provided with a holder (3) for the liquid with means for supplying or removing heat, which holder (3) is provided with a capillary structure (7) which extends above and below the liquid level. An energy system provided with at least one heat accumulator (21, 22) containing at least one heat-transporting substance which can be either in the liquid phase or in the vapour phase, and containing a crystalline material which exothermally absorbs and endothermally desorbs the heat-transporting substance, which heat accumulator has means for the supply or removal of heat (17, 18; 32, 33), contains the above installation for the heat-transporting substance, which installation is connected via a closable vapour line (16, 25) to the heat accumulator.

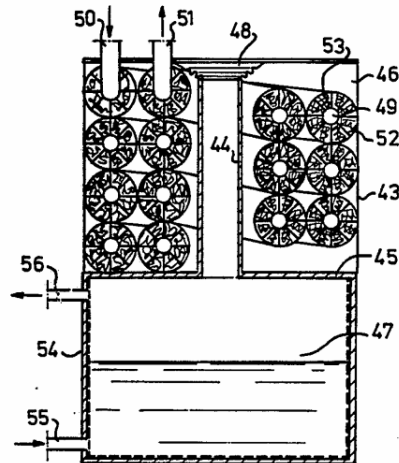


This patent is describing the same system as WO91/19154, but this time the focus is on the improvement in the evaporator by the application of a gauze (or other capillary means such as grooves or other), as well as the advantage of having the whole structure into one gastight housing to ensure that a specific atmosphere is maintained within the system.



**DeBeijer, DeBeijer Raadgevend Technisch Bureau, 1993,  
WO93/12394**

(54) Title: HEAT ACCUMULATOR, METHOD FOR THE PRODUCTION THEREOF AND ENERGY SYSTEM PROVIDED WITH SUCH A HEAT ACCUMULATOR



(57) Abstract

The invention concerns a heat accumulator consisting of a vessel having a wall (49, 52) which is at least partially heat-conducting, which vessel contains a material which exothermally absorbs and endothermally desorbs a heat-transporting substance, the absorbing and desorbing material in particular being sodium sulphide and being adhered to the wall (49, 50) of the vessel by means of a fibrous material (53), such as cellulose. Also provided is a process for the production of such a heat accumulator comprising applying a fibrous material to the inner wall of a closeable vessel, preferably via conducting protrusions, and subsequently contacting the absorbing and desorbing material being in a molten and/or hydrated state with the fibrous material.

It was found that the means of applying a layer of  $\text{Na}_2\text{S}$  as described in WO91/19154 was not sufficiently reliable and controllable. Therefore, it is proposed to use a fibrous material as a binder, such as cellulose. In addition, the new concept was found to have a better vapour transport.

The fibrous material can be brought into the vessel either in a dry state or in a humidified state. Wherever reference is made to cellulose herebelow, another fibrous can be involved as well, as explained above. If applied in a dry state, the cellulose can be brought into the vessel, optionally using a stream of air, or in the form of a powder or dust. If necessary, the fibrous material can be held in place by using a sleeve or gauze of cotton cellulose or another vapour-permeable material.

The fibrous material can also be applied in the vessel in a wet or moist state. It may then be brought in its intended place as a homogeneous paste or pulp, preferably mixed with graphite.

The fibrous material is preferably combined with an agent which improves heat conduction, such as graphite or silicon carbide. Optionally, such an agent can be applied together with the absorbing and desorbing material, but the heat-conducting material is preferably mixed with the fibrous material and applied together with the latter. The addition of graphite can - in addition to an improved heat conduction - improve the homogeneity of the structure and the stability of the layer of absorbing and desorbing material, and furthermore, the graphite can absorb possible traces of undesirable gases, such as oxygen.

Again, evaporator 47 is connected to accumulator 43 by means of pipe 44 and membrane valve 48, and separated by insulating partition 45. The active material is located on the outer area of a spiralsing heat exchanger tube

fig-5

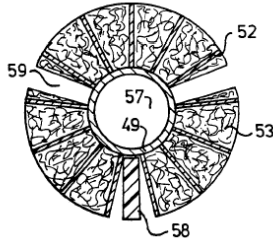


Fig. 5 represents a part of the system according to Fig. 4. In Fig. 5 a cross-section of the heat exchanging tube 49 is shown. The tube 49 encloses a space 57 for the heat transfer medium. Metal projections 52 are located on the tube. During manufacture plastic strips 58 are placed between the projections 52 in longitudinal direction of the pipe, whereafter the remaining space between the projections is filled with cellulose/graphite mixture 53. After removal of the strips 53 grooves 59 remain allowing expansions of the mass 53 to be accommodated.

EXAMPLE I

On a copper tube having a diameter of 15 mm and a length of 1.2 m, radially protruding copper hairs having a length of 10 mm were soldered with a density of about 20 hairs per cm<sup>2</sup>. Then about 100 g of a mixture of dry cellulose dust having a fibre length of 0.1 to 1 mm per fibril and graphite having an average particle size of 10 μm in a weight ratio of 50/50 was applied in the space between the hairs. A woven cotton cover was then applied around the tube containing the cellulose/graphite mixture in order to keep the cellulose/graphite mixture in place.

The tube provided with the cellulose/graphite mixture was then bent in a spiral shape and was placed in a cylindrical copper vessel having a diameter of 175 mm. The copper vessel had a concentric central tube with a diameter of 25 mm, whereby the space between the inner tube and the outer tube was closed with a disc at one end. This is shown in Fig. 4.

The ends of the spiral tube, which ends were free of cellulose/graphite mixture, was conducted through the vessel wall. The vessel was closed and liquid sodium sulphide (40% Na<sub>2</sub>S, 60% H<sub>2</sub>O) was poured into the vessel through a feed funnel. The remaining liquid was drained off from the vessel after some time; about 1000 g of sodium sulphide 40% appeared to have been absorbed to the cellulose.

The vessel was then ready for use as a heat accumulator, the spiralsing tube serving as a heat exchanger, the central concentric tube, provided with a membrane valve, serving for supply and removal of water vapour, and the sodium sulphide absorbing and desorbing water vapour.

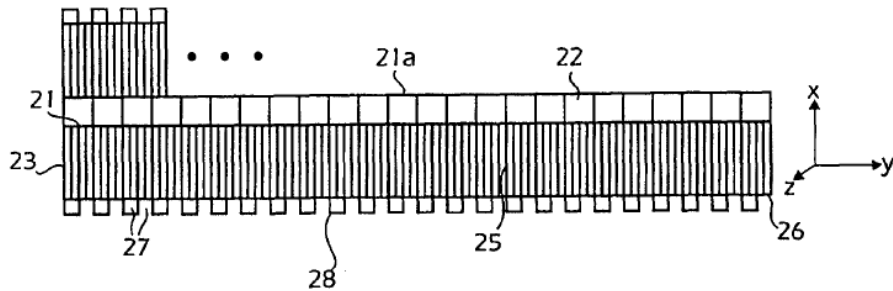
EXAMPLE II

A copper tube was provided with copper hairs in the manner described in Example I. Several plastic strips having a width of 10 mm and a thickness of 4 mm and having the same length as the copper tube were then applied between the hairs in axial direction. A 50/50 mixture of cellulose and graphite according to Example I was mixed with water into a homogeneous mass, which was subsequently applied between the hairs around the copper tube. The cellulose mass was then dried, whereby a papier-mâché-like, porous structure was obtained. The plastic strips were then removed, so that a groove free from cellulose and graphite remained. The copper tube thus coated was shaped and introduced as a heat exchanger into a copper vessel and treated with sodium sulphide as described in Example I.

Thus a heat accumulator which, as a result of a good porosity, had a satisfactory absorption and desorption of vapour was obtained.

## Jonsson, Suncool, 1999, WO 00/31206

(54) Title: A CHEMICAL HEAT PUMP USING A SOLID SUBSTANCE



### (57) Abstract

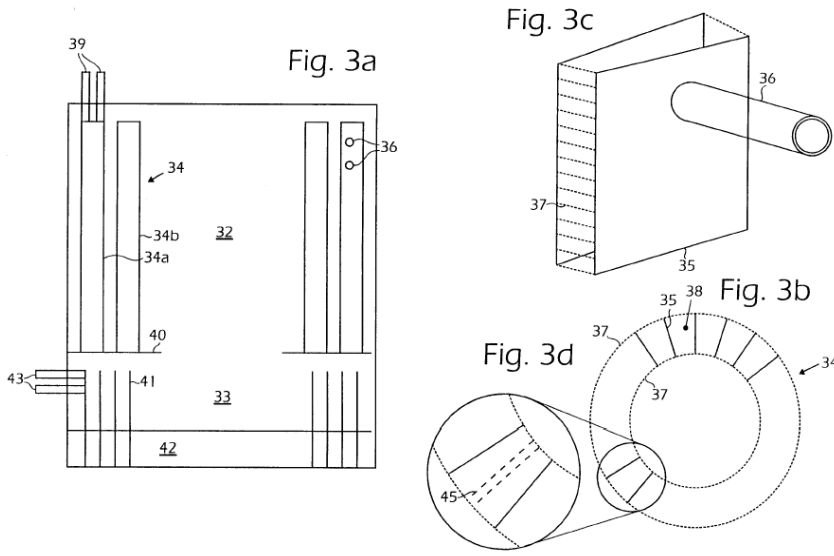
In a chemical heat pump a substance is used which in an efficient way interacts with a volatile liquid such as water. The substance is selected considering among other things the magnitude of its  $\Delta T$  and its energy content so that the heat pump becomes suited for converting low grade heat energy such as solar energy to cooling for air-conditioning and also for a simultaneous production of heat for example for use as hot tap water in houses. The heat pump can also be used in a refrigerating box. Suitable substances comprise barium hydroxide, lithium hydroxide, strontium bromide and cobalt chloride. The substance is applied as a layer (23) on the surface of a heat conducting wall (21) by applying a slurry-like mixture of the substance with the liquid when being vibrated to the wall between heat conducting flanges (25). The mixture is dried under a vacuum and is heated and is simultaneously compressed by applying an exterior pressing force. This gives a solid, well adhering layer of a substance having a high porosity which can resist a large number of cycles without any degradation of the internal structure of the layer and of its adherence to the heat conducting wall and the flanges.

With respect to the design of the system, the following information is provided:

The heat conducting structure 25 has "channels" directed perpendicularly to the surface 21 of the heat exchanger, which channels are located in the same direction as the heat and gas transport. The "channels" of this heat transport enhancing structure 25 are flanges which project perpendicularly from the heat transferring surface 21 and are rigidly attached to the surface 21. If the surface 21 would be made of copper these flanges 25 would be soldered to the surface.

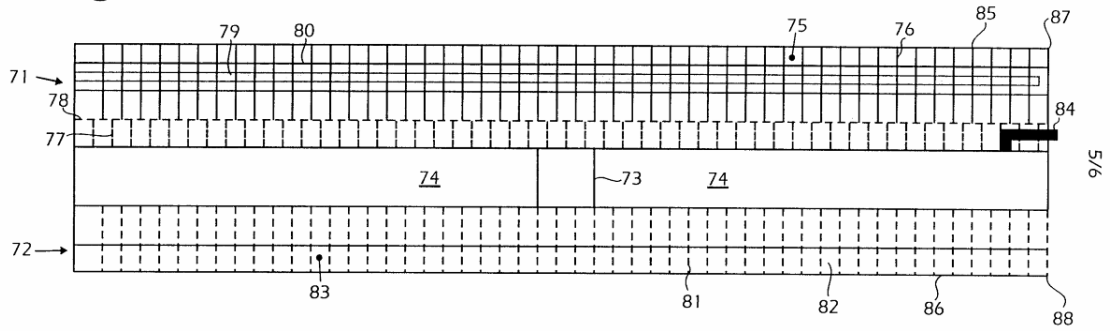
The active solid substance is applied to one surface 21 of the heat exchanger and around the structure 25 enhancing the heat transport, the substance being in the shape of a slurry mixture with water having a larger molar concentration of water than the highest working molar concentration of the substance. By vibrating the thus formed heat exchange/substance unit the mixture is attached to the surface 21 of the heat exchanger and around the structure 25 supporting the heat transport.

In a 3D layout, for reasons of strength, it is proposed to have a cylindrical evacuated tank containing a series of vertical concentric cylinder heat exchangers filled in this way with the active substance (seen in cross-section in fig 3a). The packages are thin and contain small channels (45) to facilitate the vapour flow.



As an alternative concept, also a refrigerating box for medicine transport is described:

Fig. 5



The chemical heat pump proposed herein can also be used for direct cooling purposes. It is completely possible to cool small spaces like refrigerators or refrigerating boxes for a long time. A cooling box for transport of food or medicine and having a capacity for operating for several nights and days will now be described with reference to Fig. 5.

The chemical heat pump illustrated in Fig. 5 is integrated with a lid of the cooling box, which is constructed in a way similar to the tank 31 of Fig. 3a. The lid thus has a cavity and in the interior space in the upper portion of the lid the accumulator 71 is provided which is attached to the exterior surface of the lid and in the lower part of the interior space the condenser/evaporator 72 is provided and attached to the lower surface facing the cold space of the cooling box. The accumulator 71 and the condenser/evaporator 72 are two flat, low metal containers preferably made of thin stainless steel plate, connected to each other through a centrally located tubular conduit 73 for gas transport between the accumulator 71 and the condenser/evaporator 72. They are, as to heat, separated from each other by means of a layer of heat isolating material 74 located between the accumulator part and the condenser/evaporator part. Further, the accumulator 71 is divided in two spaces, an upper space containing the substance 75 and a flange heat exchanger 76 and a lower space containing support flanges 77 made of perforated metal plate. The two spaces are separated by a close-meshed net 78. The flange heat exchanger 76 distributes heat from an electric immersion heater 79 inserted in an heat exchanger pipe 80 connected to the flanges in the flange heat exchanger 76, and forms together with the support flanges 77 in the lower part of the accumulator a support against the force of the air pressure acting on the structure. The condenser part/evaporator part 72 is filled with perforated support flanges 81 which also have the task of supporting this structure against the force of the air pressure and to conduct heat. Between the support flanges 81 a capillary sucking material 82 has been arranged, for example a cellulose material, in which the water 73 is prevented from moving freely. Evacuation of the interior space of the lid is made through a "tip-off" nipple 84 of the type used for closing for example refrigerator installations.

This patent mainly focuses on the materials selection. It provides a large amount of information on the testing results. The following selection criteria are given:

- 15 1. The substance must have a  $\Delta T$  in the range of about 20 - 40°C.
2. The substance is to react with water vapour at phase transitions having  $\Delta T$ :s close to each other.
3. The substance must at all instances in the course of the process remain in a solid state, this implying a melting point above 100°C in the preferred case. In some cases  
20 somewhat lower melting points can be allowed.
4. The substance is not allowed to sublimate.
5. The substance must be chemically stable in the reaction with water vapour.
6. The substance is not allowed to emit other gases than water vapour.
7. The substance must be mechanically stable and is not allowed to change its structure  
25 as time passes or have significant changes of its outer shape when it absorbs and emits water vapour.
8. The substance must have a high reactivity with water vapour, i.e. react rapidly, and maintain the high reactivity as time passes, for as many cycles as possible.
9. The substance must have an energy content of at least 0.15 kWh/l and preferably  
30 more.
10. The substance must be capable of being rigidly applied to surfaces of heat exchangers and is not allowed to have, as time passes, an aptitude to be detached therefrom.

A large amount of substances is subsequently discussed, among which  $\text{MgSO}_4$ ,  $\text{Na}_2\text{S}$  en  $\text{CaCl}_2$ :

Among the known substances, sodium sulphide is eliminated to be used in a solar  
25 driven heat pump both due a too high  $\Delta T$  of 58°C (characteristic 1), and due to a lacking chemical stability (characteristic 5). In a reaction with water vapour the equilibrium is displaced so that production of hydrogen sulphide  $\text{H}_2\text{S}$  cannot be avoided. This gas will then permanently exist in the system and be accumulated so that an intermittent pumping away of the gas becomes necessary. If the vapour pressure of this gas which is not desired in  
30 reaction becomes too high, the reaction speed of the water vapour with the substance in the discharging process (when the substance absorbs water) is affected and similarly the reaction speed of the water vapour in the charging process (when the substance emits water). Calcium chloride is eliminated due to a too low melting point (characteristic 3). Magnesium chloride is eliminated due to the fact that it has a too high  $\Delta T$  (54°C) in the primarily possible phase  
35 transition from 4 to 6 water molecules per molecule chloride.

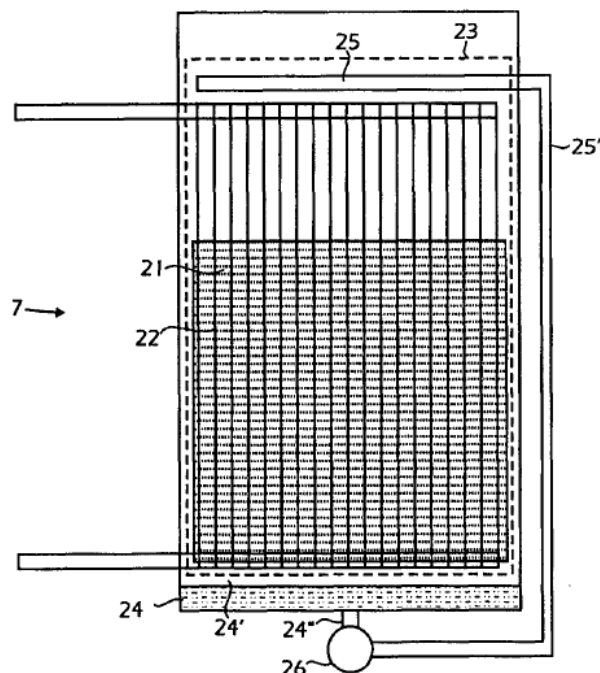
Magnesium sulphate  $\text{MgSO}_4$  could be determined to have all characteristics except 8. In tests it proved to have a reduced reaction speed in discharging, i.e. in absorbing water. This fact later appeared to be generally valid for all tested sulphates beside lithium sulphate.

## Jonsson, Suncool, 1999, WO 00/37864

(54) Title: A CHEMICAL HEAT PUMP

### (57) Abstract

In a chemical heat pump a substance is used which within the temperature range for which the heat pump is intended has a transition between a solid phase and a solution phase. The substance can for a solar driven chemical heat pump comprise magnesium chloride hexahydrate. In an accumulator part of the heat pump a heat exchanger (21) is provided enclosed by a net (23). The solid phase is primarily located inside the net in contact with the heat exchanger while the solution phase flows out of the net and is collected in a space (24') below the heat exchanger. From this space the solution phase is pumped and sprayed over the heat exchanger from a spray bar (25). Thereby, all the time the equilibrium between the solution phase and the solid phase is maintained. The advantage including the constant temperature step ( $\Delta T$ ) and the relatively large energy content of solid substances is thereby combined with the high power of liquid substances. Such a chemical heat pump is among other things suitable for converting low grade heat energy such as solar energy to cooling and in some cases also for a simultaneous production of heat.



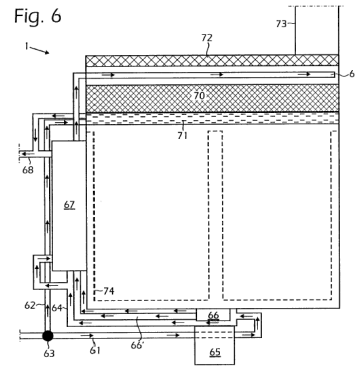
A liquid distribution system 25 is placed inside the net 23 above the heat exchanger 22 and is through a conduit 25' connected to a pump 26 so that the pump 26 can distribute solution over the heat exchanger 22. The liquid distribution system can be configured as a spray bar but it requires a rather high pressure and the small holes therein can easily be plugged by crystals formed. Instead, a rotating tube having large openings can be advantageously used.

In the designs, the use of 'surface enlarging means' is emphasised, either in the form of vertical flanges, teflon balls or other means.

When discharging the substance, i.e. when it absorbs the volatile liquid, the substance is made to be more and more dissolved in a somewhat diluted solution of the substance in the volatile liquid which exists in its vapor state around the solid and liquid phases. Thus, the produced solution is made to trickle over and through the remaining solid substance and is then passed through a filter or net to be separated from the solid substance. The solution which now becomes saturated then liberates heat produced both in the condensation of the vapor and in dissolving the vapor in the substance to a heat exchanger which is cooled by e.g. the outdoor air. This can be achieved by having a pump make the solution pass over a heat exchanger. The solution is then spread or distributed on some surface enlarging means in order to again participate in the absorption of vapor. The surface enlarging means can comprise balls, rods, nets, fibers made from some suitable material. The heat exchanger and the surface enlarging means can be combined in one unit.

As an alternative design, figure 6 is shown.

35 A somewhat different design of the reactor or absorber/generator 1 is shown in Fig. 6. In the charging stage hot water flows from a solar panel, not shown, through a suitably set valve 63 and a conduit 61 to a jacket 64 which encloses the pump 66 and a conduit 66' connecting the pump to one side of an outer heat exchanger 67. The hot water enters the other side of the outer heat exchanger 67 and continues therefrom through a conduit 68 back to the solar panel. The saturated solution flows propelled by the pump 66 driven by a pump motor 65 through said one side of the outer heat exchanger 67 to a distribution pipe 69, from which it is spread over surface enlarging means 70 arranged in the top portion of the space inside the reactor and further down over an inner heat exchanger 71, placed directly below the surface enlarging means but only having a small vertical extension and not being actively heated or cooled in this stage. At the top of the reactor a gas filter 72 is arranged and therethrough the vapor emitted from the saturated solution passes to a gas conduit 73 connected to the condenser, not shown in Fig. 6. In the evaporation crystals are formed which together with the remaining solution passes downwards at and past the inner heat exchanger 71 to the bottom of the filter or net basket 74, where they are collected, inside the basket. The saturated solution is collected at the bottom of the reactor, in a space below the bottom of the net 74.



10 The surface enlarging means can comprise Teflon balls having a diameter of 10 cm placed within a net structure at the top of the reactor space, below the top filter 72. In the illustrated embodiment, the risk of crystals being formed at non-desired places in the charging process is radically diminished, owing to primarily the flow of hot water around the pump and the conduit from the pump. Crystals can otherwise be produced in these devices, resulting in stops of the flow of saturated solution. Also, by using a closed outer heat exchanger 67 when heating the solution vapor cannot be formed and the risk of crystals being inside the heat exchanger is avoided.

15 In the total thermo-chemical heat accumulator of Fig. 7 different types of heat exchangers can be used, compare the outer plate heat exchanger 67 and the inner tube heat exchanger 70 of Fig. 6. Plate heat exchangers are used for all heat exchanging when the heat transporting medium is circulating water such as in charging in the reactors and in discharging in the evaporators. Then only the solution/water is heated in its way from the bottom of the vessel to the top. In the discharging process instead tube heat exchangers having tubes located in a zigzag fashion with long horizontal tubes are used in the reactors. The slave reactor 102 works only in discharging and thus requires only an inner heat exchanger which thus is a tube heat exchanger. In the charging step in the reactor the solution will then be heated in a closed space from which no vapor can be liberated. The solubility increases what avoids crystal formation. Only when the solution leaves the distribution pipe to flow over the surface enlarging means vapor can be liberated and then crystals can be formed. The corresponding process made in an inner heat exchanger would imply a risk for accumulation of salt crystals on the hot surfaces of the heat exchanger. In discharging in the reactor the heat exchanger is cooled what would give an obvious risk of crystal being formed in a closed plate heat exchanger. In an open tube heat exchanger inside the reactor the solution is cooled and is at the same time exposed to water vapor. Thereby, absorption of water and cooling are simultaneously made so that crystals cannot be easily formed in spite of the cooling.

Whereas the main reactor can store energy for nighttime cooling, the patent focuses on the addition of a small slave reactor to the system to provide direct cooling during daytime (see Fig 8). The slave reactor receives the charged hot saturated solution from the main reactor, to be discharged in the slave reactor, after which the diluted solution is fed back to the main reactor. In this way the slave reactor can cool continuously instead of having to be heated up periodically for charging, in which way substantial sensible heat losses, related to the heat capacity of the reactor undergoing the temperature swing, can be avoided



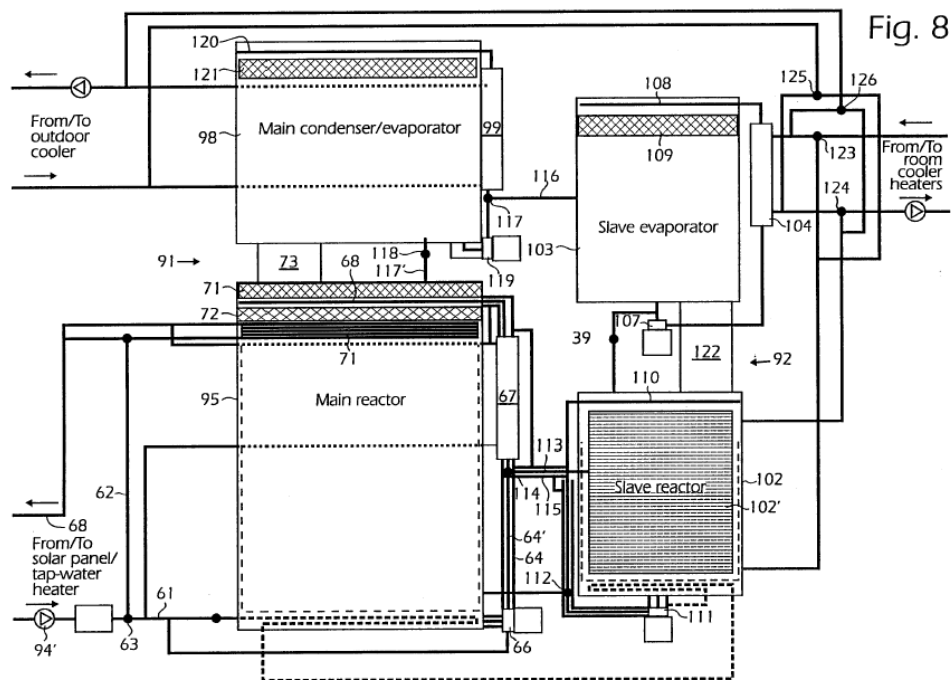


Fig. 8

Also in this patent, some information on materials is provided

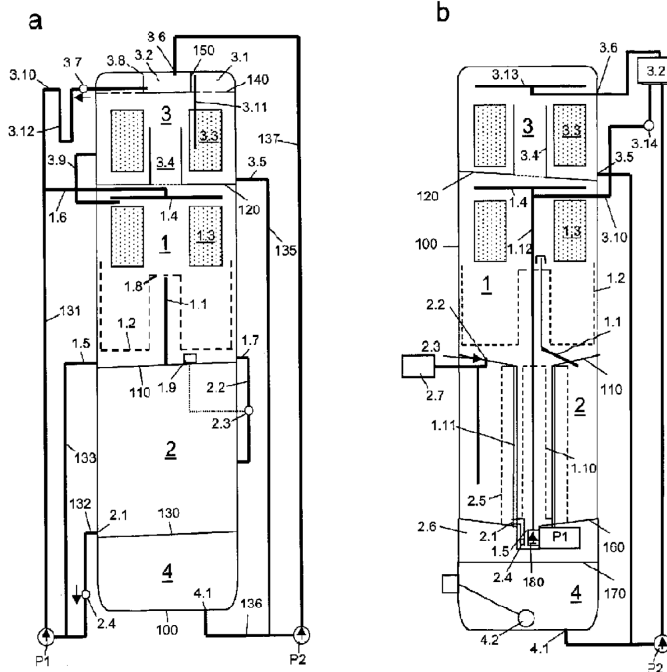
The storage capacity in kWh cooling energy per litre substance primarily depends on the  
 15 solubility of the substance in the sorbate. One mole magnesium chloride hexahydrate absorbs  
 3.5 mole water at 30°C to go into solution, which corresponds to about 0.25 kWh cooling  
 energy per litre final solution. The energy content and the temperature difference  $\Delta T$  varies  
 considerably between different substances. The corresponding calculation for  $\text{LiCl}\cdot\text{H}_2\text{O}$ , the  
 20 monohydrate of lithium chloride, gives more than 0.3 kWh/l for a temperature difference  $\Delta T$  of  
 32°C. The number of usable substances is limited. Suitable substances comprise  $\text{LiCl}$ ,  $\text{LiBr}$ ,  
 $\text{LiI}$ ,  $\text{MgCl}_2$ ,  $\text{MgBr}_2$ ,  $\text{MgI}_2$ ,  $\text{CaCl}_2$ ,  $\text{CaBr}_2$ ,  $\text{CaI}_2$ ,  $\text{SrI}_2$ ,  $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$ ,  
 $\text{AlCl}_3$ ,  $\text{AlBr}_3$  and  $\text{AlI}_3$  and among these  $\text{MgCl}_2$ ,  $\text{MgBr}_2$ ,  $\text{LiCl}$ ,  $\text{CaCl}_2$ ,  $\text{CaBr}_2$ ,  $\text{ZnCl}_2$  and  $\text{NaOH}$   
 can be considered as particularly suitable.

Also mixtures of salts can be employed. Thus, calcium chloride  $\text{CaCl}_2$  forms four  
 25 hydrates, a mono-, a di-, a tetra- and a hexahydrate. The hexahydrate is directly converted to a  
 solution when it is exposed to water vapor. However, the energy difference  $\Delta T$  is too small and  
 the energy content is small. The hexahydrate melts already at about 30°C and is thus unsuitable  
 due to a too low melting point since the temperature in the discharging processes often is higher  
 than 30°C. The substance is normally cooled by the outdoor air. The tetrahydrate absorbs water  
 30 vapor and is then directly converted to a saturated solution, provided that the temperature is  
 above 30°C and that no crystals of the hexahydrate can be formed. The melting point of the  
 tetrahydrate is about 45°C. However, the temperature difference  $\Delta T$  and the energy content are  
 too small.

However, if for example about 10% (weight)  $\text{LiCl}$  is mixed with the dihydrate, the  
 35 melting points of all the hydrates are lowered. Both the hexahydrate and the tetrahydrate will  
 then have melting points below the discharging temperatures considered herein. Then the  
 process can be run using the dihydrate (doped with  $\text{LiCl}$ ) as the start solid substance. The  
 dihydrate then absorbs water vapor passing into a saturated solution. Now an energy difference  
 $\Delta T$  equal to 26°C for a substance temperature of 30°C is obtained. The energy content counted  
 40 as cooling energy is more than 0.3 kWh per litre final solution.

## Bolin, Climatewell, 2004, WO2005/054757

(54) Title: CHEMICAL HEAT PUMP WORKING ACCORDING TO THE HYBRID PRINCIPLE



(57) Abstract: In a chemical heat pump installation two identical main units are provided, each one including a reactor and one condenser/evaporator integrated in the same container (100). One main unit is charged while the other one e.g. produces cooling. Large energy amounts are consumed in the switching operation when the unit that has been charged is to be cooled and the unit that has produced cooling is to be heated. To reduce these amounts of energy each of reactor and condenser/evaporator are divided in two further vessels. The condenser/evaporator has one part (3), in which the heat exchanger (3.3) thereof is placed, and one collecting part (4), in which the volatile liquid in its condensed shape is stored. In the same way, the reactor has a part (1), in which the heat exchanger (1.3) and the filter (1.2) thereof are placed, and a collecting part (2), in which solution of the active substance in the volatile liquid is stored. By this division only a small portion of the current mass has to change its temperature in the switching operations that hence can

be made significantly more rapidly. A large gain in cooling efficiency can be obtained in an installation having two main units. Furthermore, no valves are required on the vacuum side.

As an alternative to the slave system in the previous patent, now two identical units are used for alternating charging-discharging cycles, but the heat loss due to temperature swing is reduced in another way. It is stated that in this way, the turnaround time (during which no cooling can be provided) is lowered from 30-50 minutes to less than 10 minutes.

Furthermore, the patent focuses on the distribution system for the liquid.

A distributor or a sprayer can be pro-

vided in the reactor part to make the active substance in a liquid, i.e. in a dissolved, state pass in contact with the first heat exchanger and the solid substance. In the same way a distributor or sprayer can be provided in the condenser/evaporator part to make the volatile liquid in its liquid

30 state to pass in contact with the second heat exchanger.

In the heat pump two sprayers are used, one sprayer for spreading a solution in the reactor  
 5 part and one for spraying water in the condenser/evaporator part. These sprayers spray liquid over  
 surfaces of the respective heat exchanger and they can be designed as simple shower devices or  
 as rotating sprayer arms. In sprayers having a rotating sprayer arm driven to be rotated due to the  
 outflow of liquid, i.e. due to a reaction force, it is obtained, in the case that the flow is varying  
 and sometimes very small, which can occur in particular in the reactor part, that the sprayer arm  
 10 does not obtain any rotation movement but during more or less long time periods stands on the  
 same place and that thus all liquid flowing out then only moistens the same surfaces of the heat  
 exchanger. Instead, in order to obtain in such cases a rotation movement and distribution of liquid  
 over different surfaces of the heat exchanger, gravity can be used. Generally, such a spraying de-  
 vice can be used for spraying liquid over surfaces of an arbitrary heat exchanger.

15 A sprayer driven by gravity includes generally at least one sprayer arm that has at least one  
 outlet opening for liquid and a bearing device at which the sprayer arm is mounted to be capable  
 of rotating about a substantially vertical sprayer shaft in a rotation movement produced by the  
 flow of the liquid. The sprayer arm can be substantially horizontal or form some small angle to  
 the horizontal plane. When liquid passes out of the outlet opening in the sprayer arm, in a special  
 20 embodiment a vane or scoop device is affected that drives the sprayer arm to be rotated around  
 the rotation shaft. Particularly, the vane or scoop device can include a vane or scoop wheel that  
 has a rotation shaft and that includes at least one vane or scoop that is located so that it receives  
 liquid that is flowing out of the outlet opening. By the weight of the liquid received in the vane or  
 scoop, the vane or scoop wheel is made to rotate about the rotation shaft and then the received  
 25 liquid is emptied out over the surfaces of the heat exchanger located below the sprayer. Then, a  
 driving device is connected to the rotation shaft to make, in the rotation of the vane or scoop  
 wheel, the sprayer arm rotate about the rotation shaft of the sprayer arm.

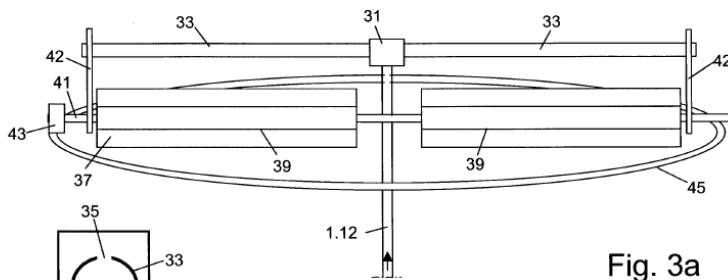


Fig. 3a

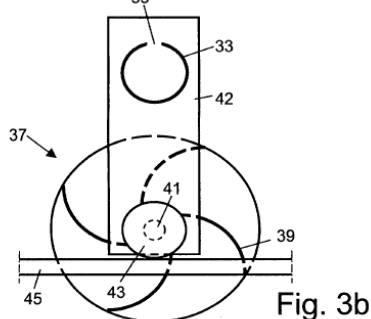
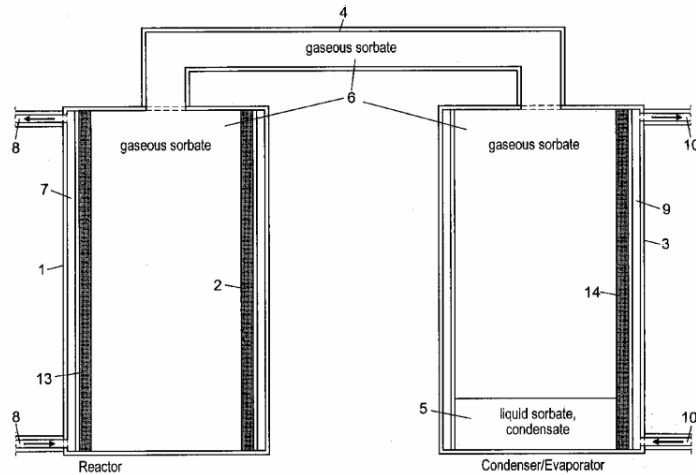


Fig. 3b

## Olsson, Climatewell, 2007, WO2007/139476

(54) Title: CHEMICAL HEAT PUMP WORKING WITH A HYBRID SUBSTANCE



(57) Abstract: A chemical heat pump includes a reactor part (1) that contains an active substance and an evaporator/condenser part (3) that contains that portion of volatile liquid that exists in a condensed state and can be absorbed by the active substance. A channel (4) interconnects the reactor part and the evaporator/condenser part. In at least the reactor part a matrix (13) is provided for the active substance so that the active substance both in its solid state and its liquid state or its solution phase is held or carried by or bonded to the matrix. The matrix is advantageously an inert material such as aluminium oxide and has pores, which are permeable for the volatile liquid and in which the active substance is located. In particular, a material can be used that has a surface or surfaces, at which the active substance can be bonded in the liquid state thereof. For example, the matrix can be a material comprising separate particles such as a powder or a compressed fibre material.

In the evaporator, also a matrix (14) is used, that draws up water by means of capillary tension, and that helps in evaporating the water.

In this patent, the advantages of using a solid switching between liquid and solid are emphasized (although the same hybrid material was also used in the previous patents).

As has been mentioned above, chemical heat pumps working with a solid substance has the disadvantage associated with a very low heat conductivity and hence a low power or efficiency and the advantages of having the ability of working without any moving parts, a high storage capacity and a constant reaction pressure. Chemical heat pumps working with a hybrid substance has the advantages of a high power or efficiency due to the higher heat conductivity and additionally, the fact that they can also work without any moving parts and that they have a high storage capacity and a constant reaction pressure.

Furthermore, the patent focuses on the matrix material in which the active material is embedded, that may be powders, fibres and/or sintered mass with a suitable porosity. It is stated that successful tests were carried out using fabrics of SiO<sub>2</sub>, or sand and glass powder.

The matrix together with the substance held therein is in this case not a solid body but a loose mass similar to wet sand in the discharged state of the heat pump. However, in the charged state of the heat pump the matrix is hard. The solution of the active substance has a significantly better heat conducting capability than the substance in the solid state thereof. Heat from the first heat exchanger 7 can then be efficiently transported to or away from the active substance. If for example a matrix consisting of aluminium oxide is filled with a 3 molar LiCl solution, a very rapid and efficient charging of the system is performed down to about a 1 molar solution. Thereafter the power decreases since the active substance now does not any longer contain any solution, i.e. does not exist in any part in a liquid phase or a solution phase. However, there is no problem to drive the process down to the concentration of 0 molar. In the discharging process the process works very well up to a state where the solution is 2.7 à 2.8 molar after which it is retarded. This is so because the matrix has not any longer any permeability to gas when the concentration of 3 molar is reached. In this condition the matrix is full, i.e. the matrix has absorbed as much solution as is substantially possible.

The function and power of hybrid systems using a solution sucked into a matrix is typically significantly better than those of solid systems. However, larger heat exchanger surfaces are required than required for systems using hybrid substances and only a free solution. Tests show that a 2 à 3 times larger heat exchanger area is required to reach, in a hybrid system using a "bonded" solution phase, the same power as in a hybrid system using only a free solution.

#### Example 1 of matrix material

A material suitable as a matrix material is produced from a powder of  $Al_2O_3$ . The density of the powder grains is  $2.8 \text{ kg/cm}^3$  and their diameter is 2 - 4  $\mu\text{m}$ . The powder is applied in layers with a solution of active substance contained therein according to the description above and the dry matrix material in the layers has a bulk density of about  $0.46 \text{ kg/cm}^3$  which gives an average filling rate or degree of the finished matrix material of 0.45, i.e. almost half the volume is taken by the powder grains. The channels between the powder grains in the produced layers have a diameter of the magnitude of order of 60  $\mu\text{m}$ .

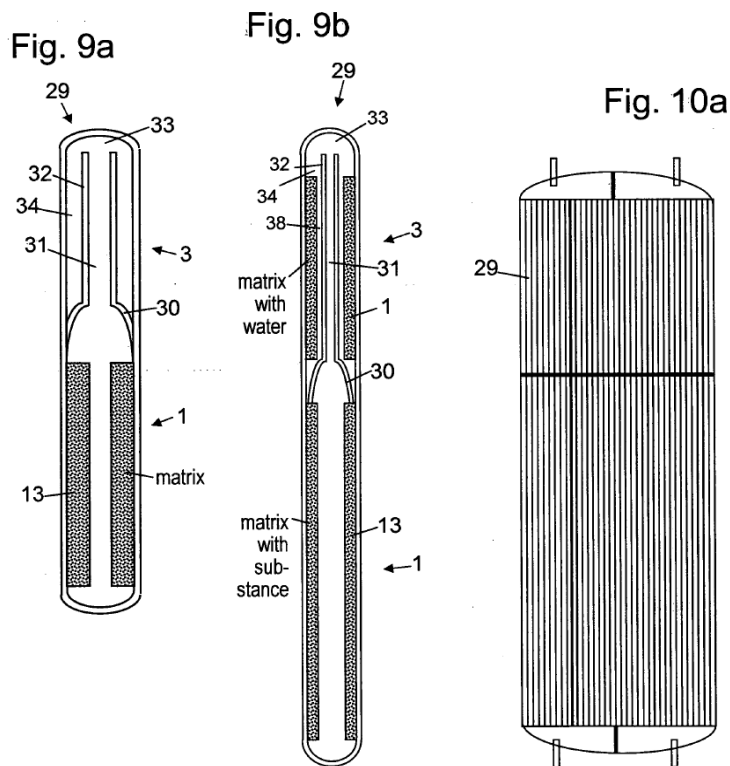
#### Example 2 of matrix material

A material suitable as a matrix material is produced by moulding a mixture of 1 (weight) part of Portland cement and 5 (weight) parts of powder of  $Al_2O_3$  as in Example 1. This material can approximately be considered as "sintered".

#### Example 3 of matrix material

A fibre material suitable as a matrix material is produced from fibres which consist of 54 %  $SiO_2$  and 47 %  $Al_2O_3$  and have a melting point of about  $1700^\circ \text{C}$ . The density of the fibres is  $2.56 \text{ kg/cm}^3$  and the diameters thereof are 2 - 4  $\mu\text{m}$ . The fibres are compressed in a wet state to increase their packing density. The bulk density after drying the compressed material is about  $0.46 \text{ kg/cm}^3$  which gives an average filling ratio of 0.17 of the finished matrix material. The channels between the fibres in the compressed material have diameters of between about 5 and 10  $\mu\text{m}$ .

Various orientations (horizontal or vertical) and shapes (see fig 9) of the basic structure are discussed in the patent, including multiple pipes (see figure 10) to increase the power.



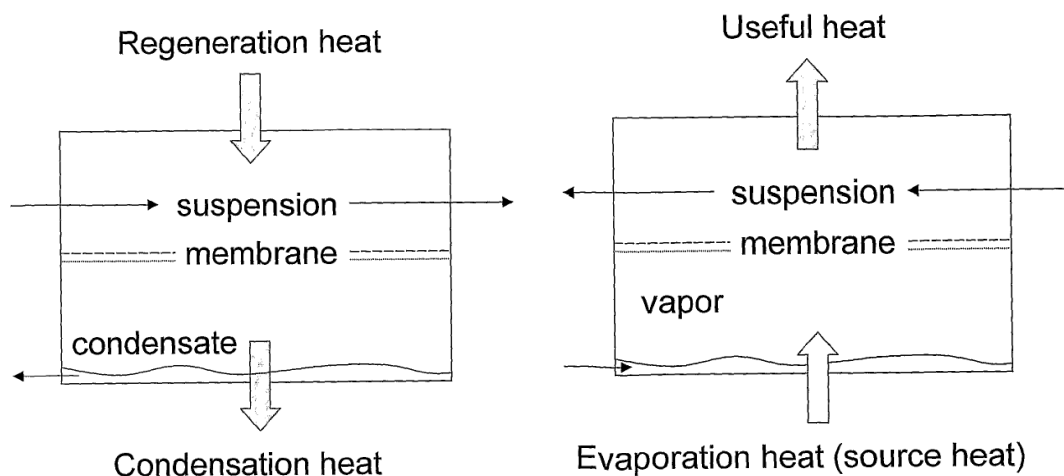
25 In another embodiment unit pipes 29 are provided in which the reactor 1 and the condenser 3 are located inside the same closed pipe. The reactor part 1 then has its matrix 2 located around the bottom portion of the interior surface of the walls, see Fig. 9a. The top portion of the pipe that forms the condenser/evaporator part 3 is separated by a diaphragm 30 from which the gas channel 31 in an interior pipe 32 passes to the top portion 33 of the pipe from which vapour then can be condensed and collected in the spaces 34 between the gas channel and the upper wall surfaces in the unit pipe and evaporate from this space. Such unit pipes can be manufactured totally hermetically from glass or enamelled steel.

## **Wemmers & Krosse, TNO, 2005, WO 2004/007633**

(54) Title: THERMOCHEMICAL HEAT STORAGE AND HEAT TRANSPORT

(57) Abstract: The invention relates to a medium for thermochemical heat storage and heat transport and to methods and apparatuses for heat storage and heat transport in which the mentioned medium is used. The invention provides a heat storage medium comprising a suspension of an adsorbent which can enter into a binding with a cold medium and is present in a suspension liquid, to which, if desired, at least one surface active substance and at least one rheology additive are added.

The patent claims the use of a suspension of a TCM. Although not explicitly claimed, the patent focuses on hydrates in a membrane concept, but it is explicitly stated that instead of water also other media such as ammonia or alcohol could be used.



The suspension is flown along a membrane, that allows diffusion of water vapour but prevents as well as possible the loss of heat.

A description of typical membranes is presented:

When both loading and unloading, the membrane provides an almost unimpeded transport of the gaseous cold medium and, simultaneously, as good a heat insulation as possible. Suitable membranes are both porous and non-porous membranes. Examples of non-porous membranes are composite or homogeneous membranes in which the active layer consists of polymers such as polyvinyl alcohol, polyacrylates, polyamides, polyethylene imine, etc. Examples of porous membranes are: PTFE, PVDF, polypropylene, polyethylene, etc. Possible ceramic membranes are, for instance, silica, aluminum oxides, zirconium oxide, etc.

In addition, requirements for the suspension are given and the use of additives is indicated to prevent sagging of the suspension..

The suspension liquid according to the invention, that is to say the continuous phase in the suspension (or the emulsion if this is formed), preferably has a mild affinity with the cold medium to promote the physical transport by the suspension liquid to the adsorbent. Moreover, the liquid preferably has a high boiling point. This limits the loss of the suspension liquid in the form of vapor, which, for instance, could disappear through the employed membrane. Furthermore, an apolar liquid is preferably used as suspension liquid. The suspension liquid is further preferably not toxic. Possible suspension liquids are phthalates, preferably dibutyl phthalate.

To prevent sagging of the solid or liquid particles in the suspension or emulsion, it is desirable in many cases to add a rheology additive, that is to say one or more substances which influence the rheology of the suspension or emulsion such that sagging of the particles, also on longer term, is prevented while the suspension remains pumpable. Preferably, the rheology additive is selected such that the suspension according to the invention behaves as a so-called Bingham liquid because this is easily pumpable. Composing such additives to prevent sagging of suspensions is known per se. Again, per adsorbent, if desired by way of routine experiments, suitable combinations of ingredients can be found to obtain a stable suspension according to the invention which does not sag. Suitable rheology additives are known to those skilled in the art.

As an example, the following suspension experimental work is presented:

A suspension according to the invention was prepared on the basis of the adsorption medium calcium chloride, the suspension medium di-n-butyl phthalate to which a dispersing agent available under the tradename of 'Disperbyk™ 2050' is added.

The suspension was prepared by dispersing partly dehydrated calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) under vacuum in the suspension liquid in which the dispersing agent was already present. Four different suspensions were prepared according to the Table below:

Raw materials	4551/35/1		4551/35/2		4551/45/1*)		4551/45/2*)	
	wt. %	vol. %	wt. %	vol. %	wt. %	vol. %	wt. %	vol. %
Dibutyl phthalate	38.5	52.2	30	41.6	38.5	52.2	30	41.6
Disperbyk™ 2050	3.8	5.2	3	4.2	3.8	5.2	3	4.2
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	57.5	42.4	67	54.3	57.7	42.4	67	54.3
Total	100	100	100	100	100	100	100	100

\*) carried out with ground  $\text{CaCl}_2$



For the absorption materials, the following is stated:

Preferably, the adsorbent is selected from the group consisting of zeolites, silicates,  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{Na}_2\text{S}$ ,  $\text{LiCl}$ ,  $\text{SrCl}_2$ ,  $\text{ZnBr}_2$ , and combinations thereof.

Furthermore, a large table of other potentially interesting adsorbents are described. Of a few of these, additional characteristics such as desorption temperatures and energy densities are provided. However, it is not clear how these data were obtained.

**Table 2. Desorption temperatures of a number of adsorbents**

Adsorbent	Molecule formula	T <sub>desorption</sub> /°C
Borax	$\text{B}_4\text{Na}_2\text{O}_7 \cdot 10 \text{H}_2\text{O}$	60-200
Gallus acid	$\text{C}_7\text{H}_6\text{O}_5$	>100
Iron (II) sulfate heptahydrate	$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	110-120
Copper (II) sulfate pentahydrate	$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	110-150
Manganese sulfate monohydrate	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	30( $4\text{H}_2\text{O}$ ) + 57/117
Sodium dichromate dihydrate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	100
Sodium peroxoborate decahydrate	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$	60-200
Sodium sulfide nonahydrate	$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	120 · (5 $\text{H}_2\text{O}$ )
Sodium thiosulfate pentahydrate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$	100*
Piperazine hexahydrate	$\text{C}_4\text{H}_{10}\text{N}_2 \cdot 6 \text{H}_2\text{O}$	104-110*
p-Sulfanil acid monohydrate	$\text{C}_6\text{H}_7\text{NO}_3\text{S} \cdot \text{H}_2\text{O}$	100
Zinc nitrate hexahydrate	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	36
Zinc sulfate heptahydrate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	280

**Table 3. Energy storage density of a number of adsorbents**

Adsorbent	Molecule formula	Energy storage / [MJ/m <sup>3</sup> ]
Calcium chloride	$\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$	258.8
Potassium fluoride tetrahydrate	$\text{KF} \cdot 4 \text{H}_2\text{O}$	480.2
Magnesium chloride heptahydrate	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	259
Magnesium nitrate hexahydrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	233
Sodium carbonate decahydrate	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	344
Sodium hydroxide monohydrate	$\text{NaOH} \cdot \text{H}_2\text{O}$	467
Sodium sulfate decahydrate	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	322.4

## Conclusions

- No specific patents were found related to the concept of a separate TCM powder reactor as examined by ECN.
- Removal of inert gasses strongly improves the system performance (Brunberg, US4186794).
- Attention should be given to the evaporator design, optimizing the active evaporation area (Climatewell, WO2007/139476).
- Matrices such as cellulose may significantly improve the mechanical stability of TCM (e.g.  $\text{CaBr}_2$ ), thereby improving the hydration conditions (DeBeijer, WO93/12394; Rockefeller, US6224842).
- In vapour absorption in a liquid, a large surface area is required, that can be obtained by various surface enlarging means (Climatewell, WO 00/37864).
- With respect to materials, several of the early patents focus on  $\text{Na}_2\text{S}$  (Brunberg, US4186794 & WO81/01726; DeBeijer, WO91/19154), but also other materials such as  $\text{CaCl}_2$  (Brunberg, US4186794),  $\text{CaBr}_2$  (for  $\text{NH}_3$ ?, Rockefeller, US6224842) and  $\text{LiCl}$  (Climatewell, for a chiller) are referred to. Suncool (WO 00/31206) gives information on the testing of a large range of materials. In particular, the patent warns against the use of  $\text{Na}_2\text{S}$  because of instability, leading to  $\text{H}_2\text{S}$  formation. For  $\text{MgSO}_4$ , the warning is given that it tends to hydrate slowly, as do most other sulfates (Suncool, WO 00/31206).