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(54) Title: MONOLITHICALLY INTEGRATED BI-DIRECTIONAL HEAT PUMP

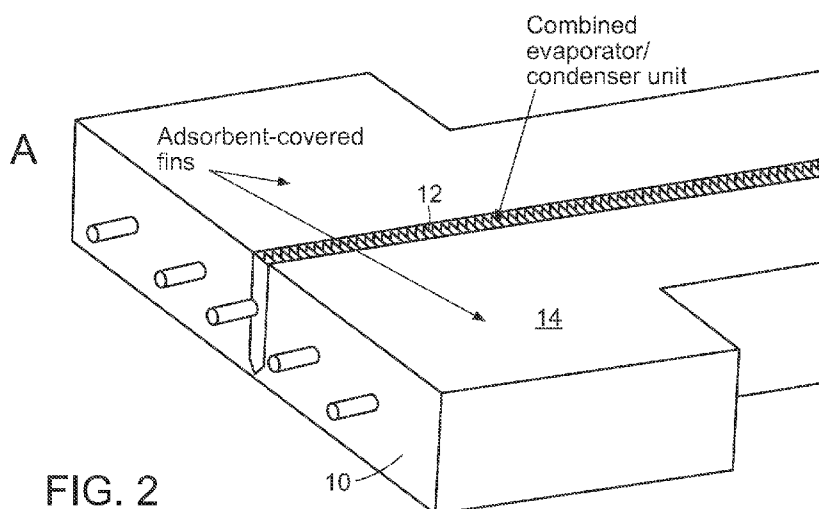


FIG. 2

(57) Abstract: Monolithically integrated heat pump. The heat pump includes an adsorbent/absorbent condenser forming a hot terminal integrated with a phase change heat exchanger forming a cold terminal. The adsorbent/absorbent condenser and the phase change heat exchanger are integrated into a single pressure vessel.

MONOLITHICALLY INTEGRATED BI-DIRECTIONAL HEAT PUMP**Sponsorship Information**

- 5 This invention was made with government support under grant no. DE-AR0000185, awarded by the Department of Energy. The government has certain rights in the invention.

Priority Information

- 10 This application claims priority to U.S. Utility Application Serial No. 14/097,401, filed on December 5, 2013 and to U.S. Provisional Application Serial No. 61/733,941, filed on December 6, 2012, the contents of which are incorporated herein by reference.

Background of the Invention

- 15 This invention relates to heat pumps and more particularly to a monolithically integrated bi-directional heat pump that integrates evaporator, condenser and adsorption bed into a single compact pressure vessel.

- Resistance to mass transfer fundamentally limits the performance of most heat pumps that
20 rely on chemical driving forces for passive operation. In the case of adsorption or absorption chillers, for example, a vapor passage constriction between the evaporator and adsorber or absorber can significantly reduce the maximum power of the heat pump. As shown in Figs. 1A and B, the mass transfer impedance severely limits the performance of some emergent heat-pump technologies, such as thermo-adsorptive batteries for electric vehicle climate
25 control that could otherwise enable significant enhancement in electric vehicle driving range [1].

- Mass transfer impedance limits the performance of some heat pump systems that use working fluids at low pressure, because of the high volumetric flow rates involved. For an adsorption
30 system using low pressure water vapor as a working fluid [1], Fig. 1 A shows the maximum heat delivery as a function of the length and cross-sectional area of the connection between the evaporator and adsorber. This calculation is based on purely diffusive transport. Fig. 1 B shows the connection geometry required to achieve 2500W heat pumping at a variety of adsorption site temperatures. While the mass transfer improves if advective transport is also

considered, this improvement comes at the cost of a pressure drop that reduces the useful temperature range of the heat pump.

5 An object of the invention is a new heat pump design which increases the effective evaporator-bed connection area and minimizes the connection length by integrating the evaporator, condenser, and adsorption bed into a single compact pressure vessel.

Summary of the Invention

10 In one aspect the invention is a monolithically integrated bi-directional heat pump having an adsorbent/absorbent condenser forming a hot terminal and a phase change heat exchanger forming a cold terminal. Both the adsorbent/absorbent condenser and the phase change heat exchanger are integrated within a single pressure vessel. The monolithically integrated bi-directional heat pump is also referred to herein as a thermal battery and other
15 similar designations.

The hot terminal of the thermal battery may comprise a packed granular or continuous material that reversibly or irreversibly physisorbs or chemisorbs the refrigerant to release heat. The hot terminal of the battery could also consist of a liquid material that reversibly or
20 irreversibly absorbs the refrigerant to release heat.

In all cases the choice of active hot-terminal material depends on the operating pressure and adsorbate. Examples of potential physisorptive materials include silica gel, zeolites, and microporous metal-organic frameworks. Examples of potential reversible
25 chemisorptive materials include activated alumina and magnesium oxides. Examples of potential irreversible chemisorptive materials include any compound that reacts exothermically with the refrigerant in the vapor phase. Examples of liquid absorbents include ammonia, lithium bromide, or hydrophilic ionic liquids.

30 In preferred embodiments of this aspect of the invention, the heat pump is liquid cooled or air cooled.

In another aspect the monolithically-integrated heat pump according to the invention includes a combined evaporator-condenser unit for bidirectional heat pumping operation,

including a first tube structure for conveying a heat transfer fluid therethrough and a second tube structure for conveying liquid refrigerant into the combined evaporator-condenser unit. An adsorbent bed is in thermal contact with a third tube structure for conveying heat transfer fluid for thermal contact with the adsorbent bed. A pressure vessel is provided to contain therewithin the combined evaporator-condenser unit, the first, second, and third tube structures, and the adsorbent bed.

In a preferred embodiment of this aspect of the invention the adsorbent bed includes adsorbent-covered fins that have microchannels engraved on their surface into which heat transfer fluid is dispensed from the third tube structure. The fins further include a structure covering the fin surface.

Brief Description of the Drawing

Fig. 1(A) is a graph of heat pump capacity versus diffusion gap for various evaporator areas.

Fig. 1(B) is a graph of required diffusion area versus diffusion length at a variety of adsorption site temperatures.

Figs. 2(A) and 2(B) are perspective views of an integrated design in a T-shape adapted for electric vehicle integration.

Fig. 3(A) is a perspective, schematic view of an evaporator fin having a porous mesh covering.

Fig. 3(B) is a cross-sectional view of a single channel in an embodiment of the invention.

Fig. 4(A) is a graph of required evaporator area versus temperature for different meshes.

Fig. 4(B) is a graph of fin height versus fin temperature.

Fig. 5 is a graph of required mass fraction uptake versus adsorbent density in a design with four 0.6 cm adsorbent coolant tubes mounted with 0.7 mm fins and with an adsorption site temperature of 80° C.

- 5 Fig. 6(A) is a schematic illustration showing heat flow and coolant/antifreeze routing for automotive cooling.

Fig. 6(B) is a schematic illustration showing heat flow and coolant/antifreeze routing for automotive heating.

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Fig. 7 is a schematic illustration showing coolant routing for a monolithically-integrated thermo-adsorptive battery during recharge.

- 15 Fig. 8 is a schematic illustration showing coolant routing for a monolithically-integrated thermo-adsorptive battery mounted thermally in parallel with a solid state heat pump bank.

Fig. 9 shows predicted adsorption site temperature on each adsorbent fin for radially-symmetric fins. This figure shows simulations for different adsorbent thermal conductivities and determines the resulting adsorbent layer thickness required to keep the maximum
20 temperature below 80° C.

Fig. 10 is a schematic illustration of a combined advective and diffusive heat and mass transfer model of the adsorption bed of an embodiment of the invention disclosed herein.

- 25 Fig. 11 are graphs of temperature or concentration against vapor gap for an embodiment delivering 2,500 W of cooling.

Fig. 12 is a graph of interfacial area versus vapor diffusivity for an embodiment delivering 2,500 W of cooling.

30

Fig. 13 is a schematic illustration of a monolithically integrated thermo-adsorptive battery with a simplified geometry.

Fig. 14 is a schematic illustration of the shape of a monolithically-integrated thermal battery designed for integration into a battery electric vehicle according to an embodiment of the invention.

- 5 Fig. 15 is a perspective view of an embodiment of the advanced thermal battery according to the invention showing a monolithic integration of an adsorption bed with an evaporator/condenser unit.

- 10 Fig. 16a is a perspective view of an embodiment of a liquid cooled adsorption bed that can be accommodated within an electric vehicle.

Fig. 16b is a perspective view of a simpler rectangular geometry of an embodiment of the invention.

- 15 Fig. 16c is a cross-sectional view of the adsorbent bed showing a centrally located evaporator/condenser (PHEX) interfaced with adsorbent on both sides.

- 20 Fig. 16d are views of a detailed design of an embodiment of the ATB showing characteristic dimensions of sub-components. The front view shows characteristic dimensions and arrangement of coolant types, adsorption bed and phase-change heat exchange. The top view shows the characteristic thickness and arrangement of the adsorption stacks on both sides of the phase change heat exchanger.

- 25 Fig. 17 is a graph of adsorption capacity versus density of adsorbent for a fixed overall volume of the advanced thermal battery disclosed herein.

Fig. 18a is a graph of net vapor adsorption versus time showing temporal variation in net vapor adsorption.

- 30 Fig. 18b is a graph of average temperature versus time showing average adsorbent temperature during the first 60 minutes of operation of an adsorbent delivering 30 weight percent vapor adsorption capacity at 760 Pa and 80 degrees C. The overall average rate of adsorption was approximately 0.0011 kg/s.

Fig. 19a is a graph of average adsorbent temperature versus antifreeze/coolant HTC showing the average temperature distribution of adsorbent as a function of its thermal conductivity and heat transfer coefficient of the coolant.

- 5 Fig. 19b is a graph of pumping power versus antifreeze HTC showing pumping power required for circulation as a function of the heat transfer coefficient.

Fig. 20 is a graph of relative pressure versus antifreeze/coolant temperature between 303 K (30 degrees C) and 333 K (60 degrees C), which represent typical conditions that can be
10 expected during mild summer and winter.

Fig. 21 is a view of a single cell or “button cell” embodiment of the present invention.

- Fig. 22 are perspective views of a button cell embodiment showing a hot terminal of Zt 13x
15 compressed in an aluminum honeycomb and a cold terminal including a porous media evaporator and bare condenser plate connected to a reservoir.

Figs. 23 and 24 are perspective views of an adsorbent test station showing Zt 13x thermo-compressed in aluminum honeycomb.
20

Fig. 25 comprises views of the evaporator side of the ATB showing 10x compressed 95% porosity copper foam having approximately 110 μm pore sizes and also shows the liquid directed to minichannels beneath the porous copper.

25 Description of the Preferred Embodiment

An embodiment of the invention is shown in Figs. 2(A) and (B). Fig. 2(A) shows the integrated design in a T-shape particularly adapted for battery electric vehicle integration. The integrated design 10 includes a combined evaporator-condenser unit 12 along with
30 adsorbent-covered fins 14. In the exploded view of Fig. 2(B), showing the adsorbent material mounted on liquid-cooled fin tubes, arrow 1 indicates the flow of heat transfer fluid to the evaporator-condenser 12. The arrow 2 indicates the flow of liquid refrigerant into the evaporator-condenser unit during battery discharge. Arrow 3 indicates the flow of heat

transfer fluid to the adsorbent fins. The pressure vessel containing these elements is not, itself, shown for the sake of clarity.

The monolithically-integrated design disclosed herein combines three separate subsystems from traditional adsorption heat pumps—the evaporator, condenser, and adsorbent bed, into a single pressure vessel. This consolidation increases the planned connection area by nearly 200x, from $.0008 \text{ m}^2$ in a traditional duct-based system to $.136 \text{ m}^2$, and decreases the mean connection length from approximately $.2 \text{ m}$ to $.076 \text{ m}$, thereby addressing the mass transfer impedance challenges that have hampered previous efforts to develop compact, energy dense adsorption heat pumps. Additionally, the consolidation to a single pressure vessel comes at an estimated system volume savings of 4.5 L from a conventional design by eliminating the evaporator and condenser subunits, as well as associated brackets and tubing.

Any thermal leak is mitigated by ensuring minimal contact between the adsorption bed and the combined evaporator/condenser in this design (as shown in Figure 2). Thermal leakage can take place due to heat conduction through the vapor phase separating the adsorption-bed and the evaporator, and conduction through the coolant pipes that connect the adsorption bed and the pressure vessel. This thermal leak through the vapor is estimated to be less than 1 W during bed operation, based on the low thermal conductivity of $.01 \text{ W/mK}$ of steam at 710 Pa . The thermal leak through the endwalls is estimated to be 6 W based on $.001 \text{ m}$ thick stainless steel walls and thermally insulated, $.01 \text{ m}$ diameter KF-type (vacuum) pipe fittings.

The combination of the evaporator and condenser units into a single fin structure requires the development of a surface that is conducive to both thin-film evaporation and either filmwise or dropwise condensation. A design is shown in Fig. 3. In the cooling mode, wherein the evaporator is utilized, liquid water is dispensed into microchannels engraved on the surface of the fin from refrigerant lines running through the evaporator fins. Water spreads through the microchannels, and fills a wick structure covering the fin. This wick structure serves to enhance thin-film evaporation [2] and provide the pressure gradient necessary for evaporation that would otherwise be provided by an expansion valve or capillary. Filmwise or dropwise condensation also occurs on this wick structure, which will consist of a multi-layered sintered copper or aluminum wick. The condensate is collected in a

trough at the bottom of the fin and is routed out of the bottom of the integrated pressure vessel.

Based on a conservative filmwise condensation model [3] as shown in Fig. 4A, a 4 cm tall condenser fin that spans the length of the bed could facilitate recharge within 2 hours with a 40 °C condenser temperature. Based on the heat fluxes observed in [2] and a 1 mm copper mesh wick structure, the evaporator should be sized as shown in Fig. 4B.

The design disclosed herein allows more volume for adsorbent material than traditional systems, as a result of the consolidation of the evaporator and condenser to a single structure, and the elimination of bulky ducting and local air heat exchangers. As a result, the mass percent uptake required to reach a 4500 W heating benchmark for automotive integration varies with the adsorbent density and acceptable adsorbent site temperature as shown in Fig. 5. For comparison, the required uptake for an identical chiller using a conventional modular design ranges from 50-80%. In the figure, four 0.6cm adsorbent coolant tubes were mounted with 0.7mm fins and with an adsorption site temperature of 80°C.

As shown in Figs. 6 and 7, the combination of all system components into a single pressure vessel is conducive to integration with pre-existing automotive heat exchange structures via simple valve structures.

Fig. 6A shows heat flow and coolant/antifreeze routing for automotive cooling. Fig. 6B shows heat flow and coolant/antifreeze routing for automotive heating.

The monolithically-integrated design disclosed herein is also conducive to integration with a secondary heat pump system, as shown in Fig. 8. This type of integration could be of interest in mobile applications, in which the system may occasionally be required to supply more heating or cooling than the adsorption system can store.

Based on the energy density of a typical electric vehicle primary battery bank (.234 MJ/L) and the heat pump COP of commercially-available Peltier units (1.8 heating, 0.6 cooling), a vehicle climate-control system based on solid-state heat pumps would be approximately 40-60% as energy-dense as the adsorption-based system in [1] (9MJ heating or

cooling in 30L). However, due to the small size of the Peltier units themselves (0.1L), they may represent a space-efficient means to increase the maximum power and endurance of the ATB system. Because the Peltier units draw power from the primary battery, the units effectively only displace volume electric vehicle only when they are in use, unlike an adsorption system. In all, integration with a secondary solid-state heat pump could allow the system more flexibility for occasional overloads that the adsorption system alone could not handle.

While many details of heat and mass transfer for this design remain to be established, the adsorbent temperature can be estimated based on assumed radiator and heater core heat exchanger efficiencies. Assuming $\eta_{\text{Radiator}} = \eta_{\text{Heater Core}} = 0.9$ and four 1 cm diameter adsorbent coolant pipes as depicted in Fig. 2, the average coolant temperature in the adsorbent cooling tubes could be kept at approximately 70 °C with an adsorbent temperature profile on each fin as shown below. This configuration would require an estimated 40 W of pumping power for the circulation of a coolant or antifreeze. Fig. 8 shows the expected temperature distribution across the adsorbent based on these assumptions for fins mounted with adsorbents with different thermal conductivities ranging between 0.3 to 5 W/mK. For these computational simulations, the volumetric heat generation is assumed to be a constant 126 kW/m³, corresponding to an overall heat delivery of 2500 W. Because the heat of adsorption is higher than the heat of evaporation, the adsorbent temperature will likely be higher than that shown in Figure 8, during a 2500 W cooling operation.

Fig. 9. shows predicted adsorption site temperature on each adsorbent fin as drawn in Fig. 1 for radially symmetric fins. The maximum temperature is held to 80 °C, the coolant flow is at the system average of 70 °C through 0.6 cm pipes, and the fin thickness is 0.7 mm. The figure shows simulations for different adsorbent thermal conductivities κ_r and determines the resulting adsorbent layer thickness t_{ad} required to keep the maximum temperature below 80 °C. Note that the vertical axis of each figure is in millimeters, while the horizontal axis is in meters.

The monolithically-integrated adsorption heat pump system was analyzed using a 1-D model incorporating both advective and diffusive heat and mass transfer between the system hot and cold sides. A schematic view of this model is shown in Fig. 10. Based on a 2500W cooling deliver benchmark, the design will operate as shown in Figs. 11 and 12, with a net

thermal leak of $\sim 15\text{W}$ including conduction, diffusion, convection, and radiation, based on a stainless steel vessel and emissivity ϵ of .2 for the adsorbent material.

Possible risks of the monolithically integrated design include a thermal leak between
5 the evaporator and adsorption bed during bed discharge, additional entropy generation
associated with the intermediate antifreeze-air heat exchangers, and the possibility of boiling
the antifreeze during the high temperature system recharge.

The evaporator/condenser and adsorption bed will be thermally isolated from one
10 another by non-conductive KF-type vacuum fittings between the coolant pipes and the
pressure vessel enwalls. These fittings represent the only thermal contact between the two
subsystems. If this thermal resistance is found to be insufficient, additional isolation can be
achieved by fabricating the pressure vessel from a relatively thermally insulating material,
such as stainless steel.

15 While some additional temperature drop between the ATB system and the passenger
cabin is inevitable with the intermediate heat exchange step in the heater core, the
temperature drop is estimated between 2 and 6°C based on the efficiency of typical
automotive heater cores. This temperature drop is offset by the additional adsorption capacity
20 afforded by the liquid cooling strategy.

Since typical zeolite desorption temperatures exceed the boiling temperature of most
liquid coolants, coolant boiling in the antifreeze line is possible during system recharge.
Boiling within the coolant lines can be minimized either by draining the coolant line prior to
25 recharge, or by allowing for some volume expansion using a venting mechanism within the
coolant reservoir.

Another risk associated with all heat pump systems that use water as a working fluid
is refrigerant freezing in very cold temperatures. This risk might be avoided by using a
30 mixture of an alcohol (such as methanol) and water as the working fluid. In this way, freezing
can be avoided without significantly impacting heat delivery capacity, as many alcohols are
also useful as adsorbates. Moreover, if the liquid mixture is near the azeotropic point, the

evaporator temperature can be made lower during system discharge, increasing the effectiveness of the heat pump system.

A planned prototype with a simplified 'button cell' heat transfer geometry is shown in Fig. 13. The button cell design will be discussed further below.

While further modeling is required to validate the monolithically-integrated bi-directional heat pump structure presented in the document design, these preliminary calculations indicate that the revised design can greatly enhance the energy density of a thermo-adsorptive battery system by 1) reducing the system volume by combining three different system components, 2) eliminate mass transfer resistance between the evaporator/condenser units, and the adsorption bed, and 3) streamlining vehicle integration by utilizing pre-existing heat exchange infrastructure (radiator and heater core) and incorporating smaller and more flexible liquid coolant lines in place of air ducts.

A T-shaped embodiment of the invention is shown in Fig. 14 and is suited for automotive use.

The overall design of an embodiment of the advanced thermo-adsorptive battery is illustrated in Fig. 15 (not drawn to scale). The ATB consists of an adsorption bed monolithically integrated with a phase-change heat exchanger (PHEX) serving as an evaporator as well as a condenser. During the ATB discharging process the PHEX is used as an evaporator, while it is used as a condenser during ATB recharge process. The adsorption bed and the PHEX are thermally interfaced with coolant lines for supplying or rejecting heat from the ATB. The adsorption bed is composed of several rows of adsorbent stacks with minimal spacing to allow vapor transport. Each stack consists of thin adsorbent layers attached to metallic substrates that are in contact with the coolant lines. This arrangement minimizes the net thermal resistance for heat dissipation from the adsorption bed to the coolant. The evaporator/condenser is constructed using a porous media to provide a large surface area for evaporation and condensation of water during ATB discharge and recharge process, respectively. A refrigerant line supplies liquid water, while multiple coolant lines allow exchange of heat with the evaporator/condenser unit. During ATB discharging process, water is pumped from a reservoir to the evaporator. The vapor generated due to evaporation diffuses into the bed, where it is adsorbed. During summer, the evaporator provides cooling

and during winter the adsorption bed delivers heating. The adsorption bed is regenerated by providing heat which causes vapor desorption. The desorbed vapor diffuses back into the PHEX, which functions as a condenser for the regeneration mode. The condensate collected in the ATB is transported back into the reservoir for subsequent use. Note that the reservoir is
5 externally located and not shown for clarity.

An embodiment of the invention, particularly adapted for electric vehicle integration, is shown in Figs. 16a, b, c and d. The characteristic dimensions and arrangement of various sub-components within the ATB including the coolant tubes, the adsorption bed and the
10 PHEX are shown in this figure. A total of 8 coolant lines are interfaced with each half of the adsorption bed to dissipate the heat released during adsorption of vapor. The adsorption bed consists of multiple rows of stacks, with each stack representing a metallic fin attached with thin layers of mechanically-compressed adsorbent. The gap between the rows of stacks facilitates efficient transport of vapor between the evaporator and the adsorption bed, and
15 allows maximum utilization of the adsorbent in the desired operational duration. The heat generated during adsorption is conducted across the thin adsorbent layers to the thermally conductive metallic fin which dissipates heat to the coolant line. Consequently, the design allows efficient heat and mass transfer to deliver high energy and power density for climate control in electric vehicles. It should be noted that Fig. 16 is an optimized design for the use
20 of ATB in the electric vehicles. However, with minor modifications in the dimensions and form factor, a similar arrangement of sub-components can be utilized for various applications desiring temperature control, e.g. heating and cooling in buildings, storage and transport of heat sensitive materials such as medical supplies, organs, biological specimens etc.

25 In order to deliver a net heating and cooling capacity exceeding 2.5 kW, Fig. 17 shows the required adsorption capacity as a function of the average packing density of the adsorbent for the design illustrated in Fig. 16 using water as a refrigerant. For instance, with an average packing density of 850 kg/m^3 , a net vapor uptake of $\sim 0.3 \text{ kg}_{\text{vapor}}/\text{kg}_{\text{adsorbent}}$ or 30 wt.% is required to deliver $\sim 2.5 \text{ kW}$ of heating and cooling. The average packing density also
30 determines the total mass of adsorbent inside the ATB. For instance, with a packing density of 850 kg/m^3 , the ATB utilizes close to 19 kg of adsorbent.

With a detailed computational analysis of adsorption dynamics, the performance variation of ATB over time can be predicted. Using an adsorbent that delivers a 30 wt. %

vapor adsorption capacity at low vapor pressures (~ 760 Pa) the ATB performance variation over 60 minutes of operation is shown in Figs. 18a and b. Starting with dry conditions, the initial rate of adsorption of vapor is quite high when ATB is exposed to a constant vapor pressure of 760 Pa. However, due to saturation, the rate of vapor adsorption is gradually diminished, as shown in Fig. 18(a). This variation in the rate of vapor adsorption results in an initial spike in the temperature of the adsorbent followed by a gradual decrease, as shown in Fig. 18(b). In the actual implementation of the ATB, the refrigerant supply to the evaporator will be controlled using a flow control valve. This will regulate the pressure inside the ATB to provide a steady operating condition. The detailed computational analysis also shows that an adsorbent with 30 wt.% adsorption capacity at 760 Pa will provide an average heating and cooling rate exceeding 2.5 kW for a duration of 1 hour when it is incorporated into the design illustrated in Fig. 16(d).

In order to determine the operating conditions to deliver the required uptake shown in Fig. 18, it is necessary to determine the temperature distribution within the bed during operation. Figs. 19a and b show the average bed temperature as a function of the thermal conductivity of the adsorbent and the heat transfer coefficient (HTC) provided by circulating the coolant in the coolant lines (see Figs. 15 and 16 illustrating the coolant flow arrangement). This corresponds to a uniform rate of heat generated (0.23 MW/m^3) in the adsorption bed. Clearly, the bed temperature can be lowered if the thermal conductivity and the HTC are both increased. While the HTC can be increased at the expense of higher pumping power (Fig. 19(b)), a higher thermal conductivity can be obtained using high-k binding materials. In order to minimize the overall thermal resistance between the bed and the coolant, a thermal conductivity $>1 \text{ W/mK}$ is desirable.

A higher thermal conductivity resulting in a lower operational temperature is essential to maximize adsorption during ATB operation. Fig. 20, shows the relative pressure as a function of thermal conductivity and the coolant temperature. The temperature of the coolant depends on the ambient weather conditions. In this regard, the most challenging operating conditions for adsorption correspond to the winter, wherein the coolant providing heating to the EV cabin has to be maintained at a temperature of 60°C . This operating condition corresponds to a relative pressure of $\sim 2\%$, if the average thermal conductivity of the adsorbent is 1 W/mK . In summary, an adsorbent packing density of 850 kg/m^3 , thermal conductivity of 1 W/mK , and an adsorption capacity of 30 wt.% at a relative pressure of 2%,

will deliver heating and cooling in excess of 2.5 kW using the ATB design illustrated in Fig. 16.

While water is the preferred refrigerant due to superior thermophysical properties, it is also environmentally benign and safe for applications. However, freezing of water is detrimental to the overall performance of the device. Consequently, in the actual ATB application, water is added with methanol to avoid freezing. Apart from reducing the freezing point of the refrigerant methanol is also adsorbed by the adsorption bed.

A single cell or “button cell” embodiment of the invention will now be discussed in conjunction with Figs. 21-25.

Fig. 21 shows the overall integrated design for this embodiment. As shown in Fig. 22, one side is a hot terminal comprising Zt 13x compressed in an aluminum honeycomb and a cold terminal including a porous medium evaporator and bare condenser plate connected to a reservoir, in this case a 120 ml reservoir.

Figs. 23 and 24 show more detail of the compressed aluminum honeycomb.

Fig. 25 shows the evaporator side including 10x compressed 95% porosity copper foam having approximately 110 μm pore size. Minichannels serve to direct liquid beneath the porous copper. As shown in Fig 13, the ATB is a heat pump that can be charged and discharged like a battery. The unit is charged up by applying a temperature difference to the terminals. The temperature difference can be recovered at a later time by opening a valve connecting a reservoir to the adsorbent bed.

The numbers in square brackets refer to the references listed herein. The contents of all of these references are incorporated herein by reference in their entirety.

It is recognized that modifications and variations of the present invention will occur to those of skill in the art, and it is intended that all such modifications and variations be included within the scope of the appended claims.

REFERENCES

[1] See original technology disclosure for MIT Case 15230

[2] Chen Li et al., Evaporation/Boiling in Thin Capillary Wicks—Wick Thickness Effects,
5 Transactions of ASME 2006, 128(1).

[3] Frank Incropera, Fundamentals of Heat and Mass Transfer, Wiley 2002.

[4] Ernst-Jan Bakker and Robert de Boer, Development of a 2.5kW Adsorption Chiller for
Heat-Driven Cooling, Energy research Centre of the Netherlands 2008.

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What is claimed is:

- 1 1. Monolithically integrated heat pump comprising:
2
3 an adsorbent/absorbent condenser forming a hot terminal;
4
5 a phase change heat exchanger forming a cold terminal; and
6
7 a pressure vessel, wherein the adsorbent/absorbent condenser and the phase change
8 heat exchanger are integrated within the pressure vessel.
- 1 2. The heat pump of claim 1 wherein the heat pump is liquid cooled.
- 1 3. The heat pump of claim 1 wherein the heat pump is air cooled.
- 1 4. Monolithically integrated heat pump comprising:
2
3 a combined evaporator-condenser unit for bi-directional heat pumping operation
4 including first tube structure for conveying a heat transfer fluid therethrough;
5
6 a second tube structure for conveying liquid refrigerant into the combined evaporator-
7 condenser unit;
8
9 an adsorbent bed in thermal contact with a third tube structure for conveying heat
10 transfer fluid for thermal contact with the adsorbent bed; and
11
12 a pressure vessel containing therewithin the combined evaporator-condenser unit, the
13 first, second, and third tube structure, and the adsorbent bed.
- 1 5. The heat pump of claim 4 wherein the adsorbent bed includes adsorbent-covered fins.
- 1 6. The heat pump of claim 5 wherein the fins have microchannels engraved on their surface
2 into which liquid water is dispensed from the third tube structure.

- 1 7. The heat pump of claim 5 wherein the fins further include a wick structure covering the fin
- 2 surface.

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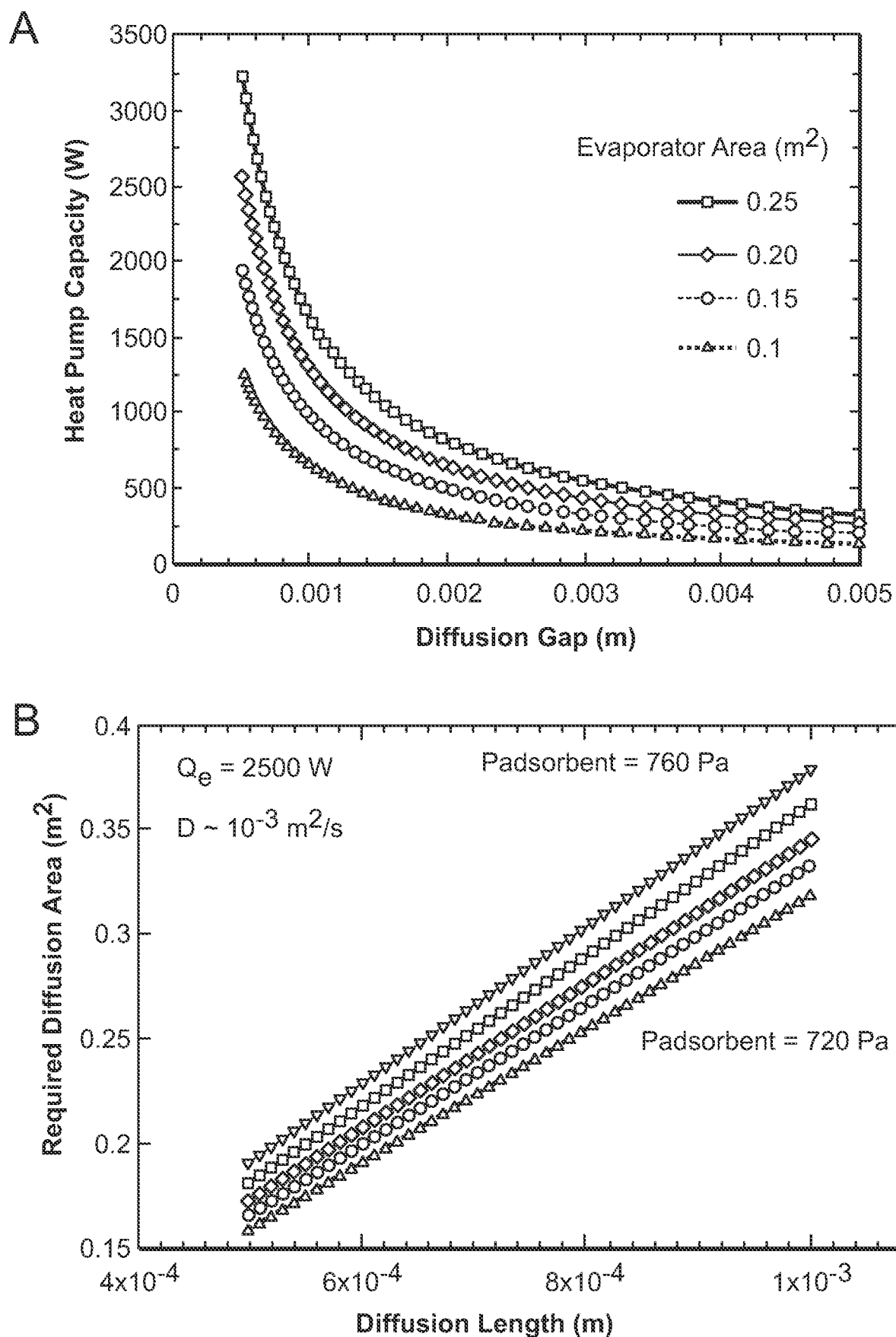


FIG. 1

SUBSTITUTE SHEET (RULE 26)

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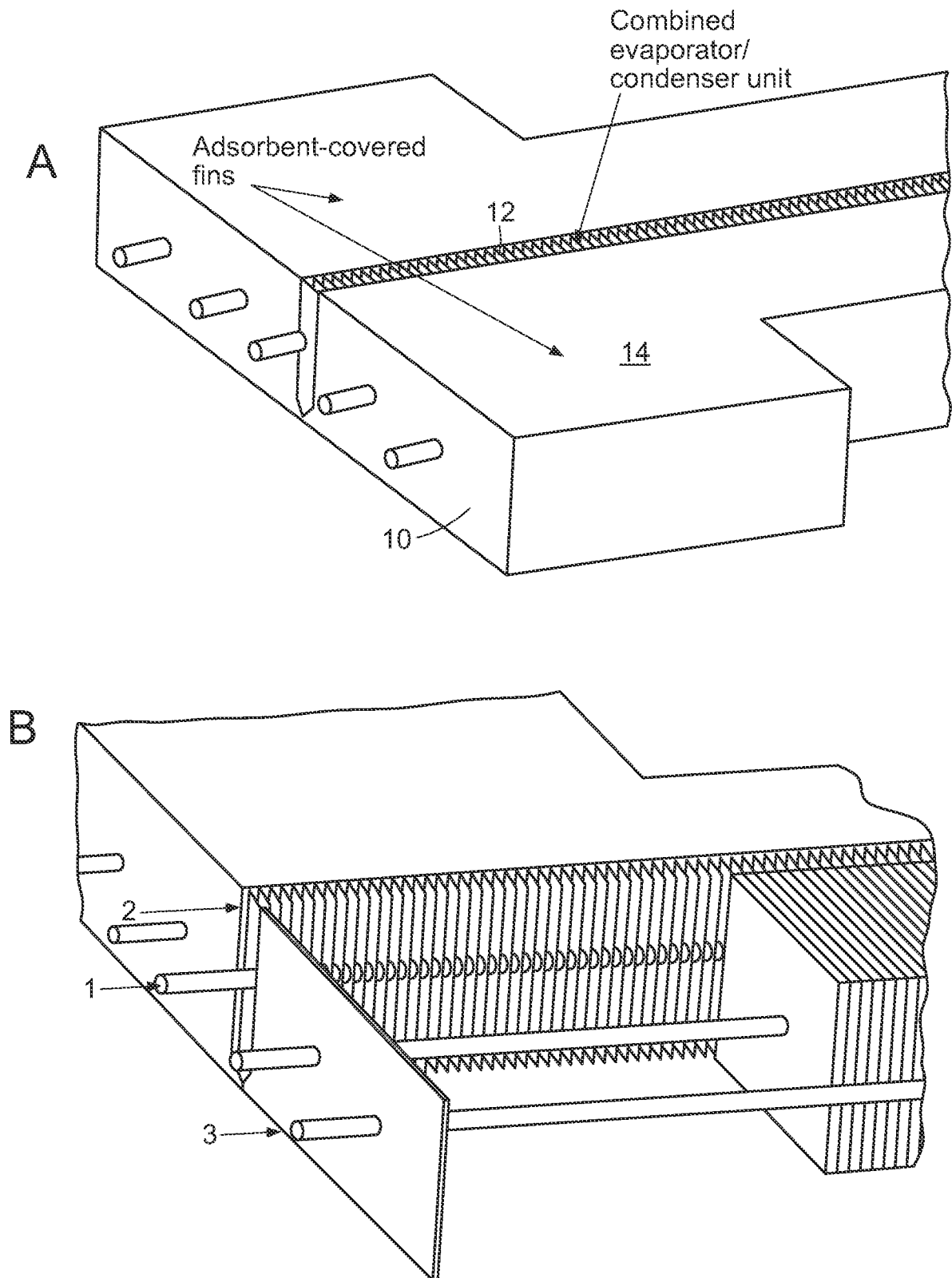


FIG. 2

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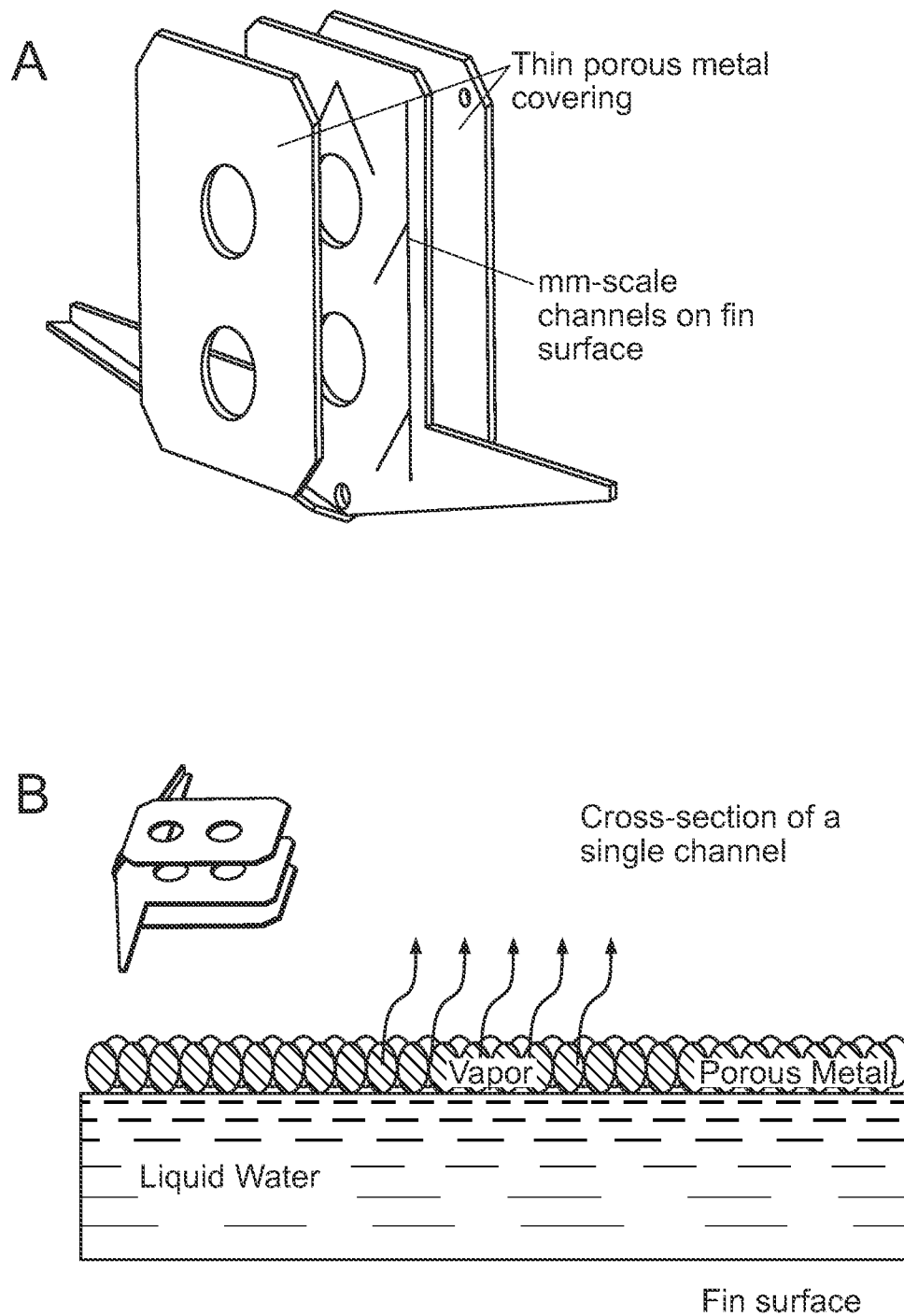


FIG. 3

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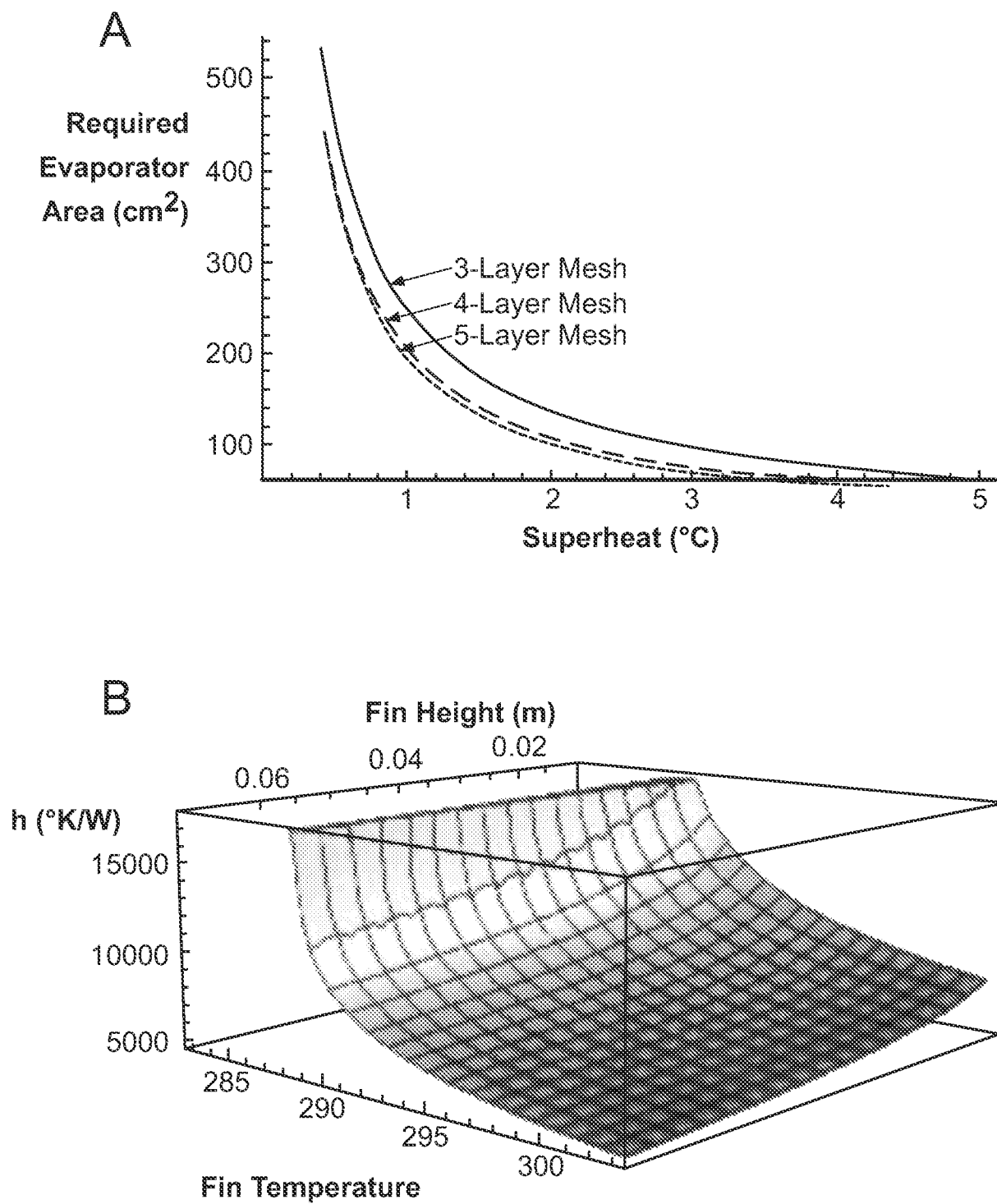


FIG. 4

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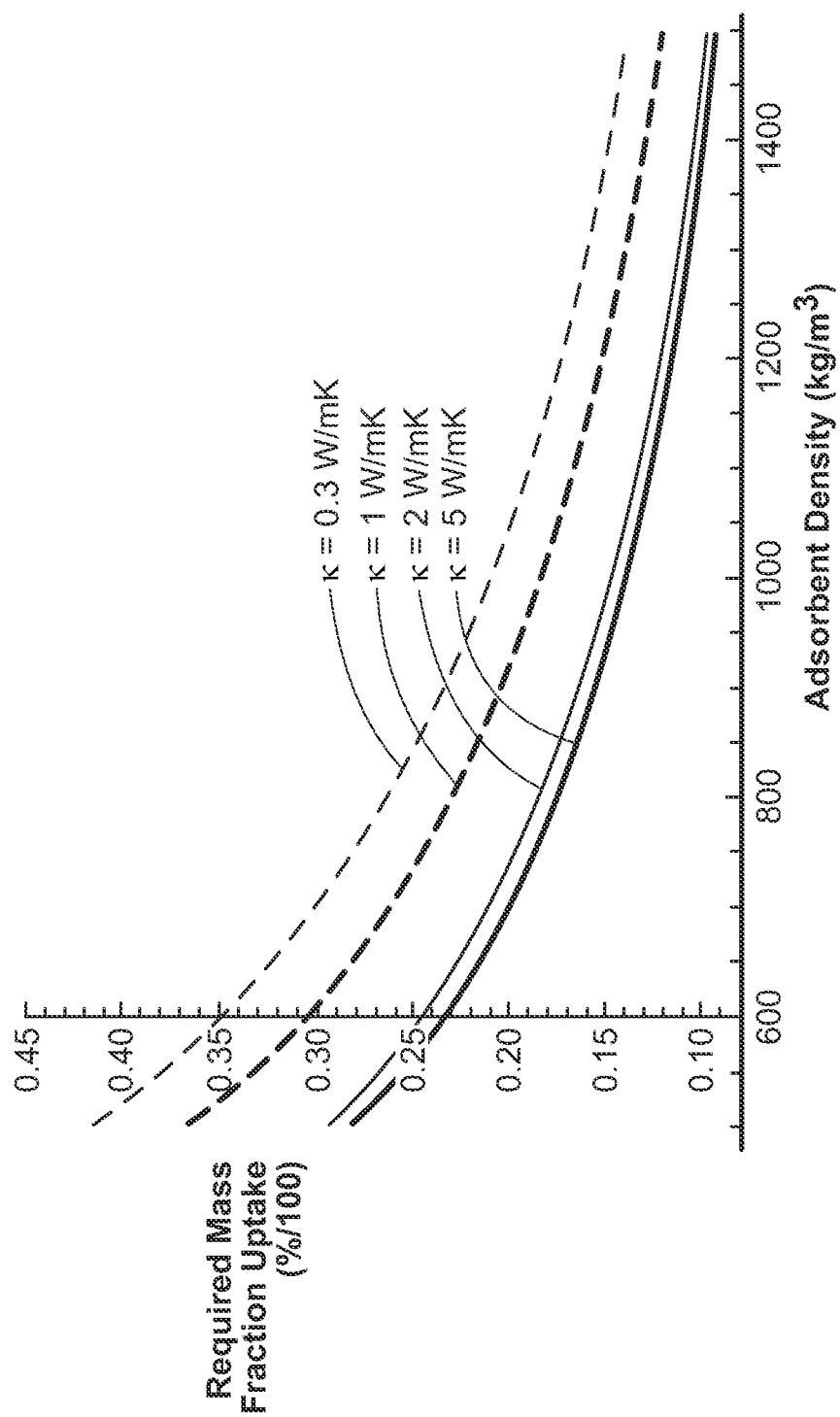


FIG. 5

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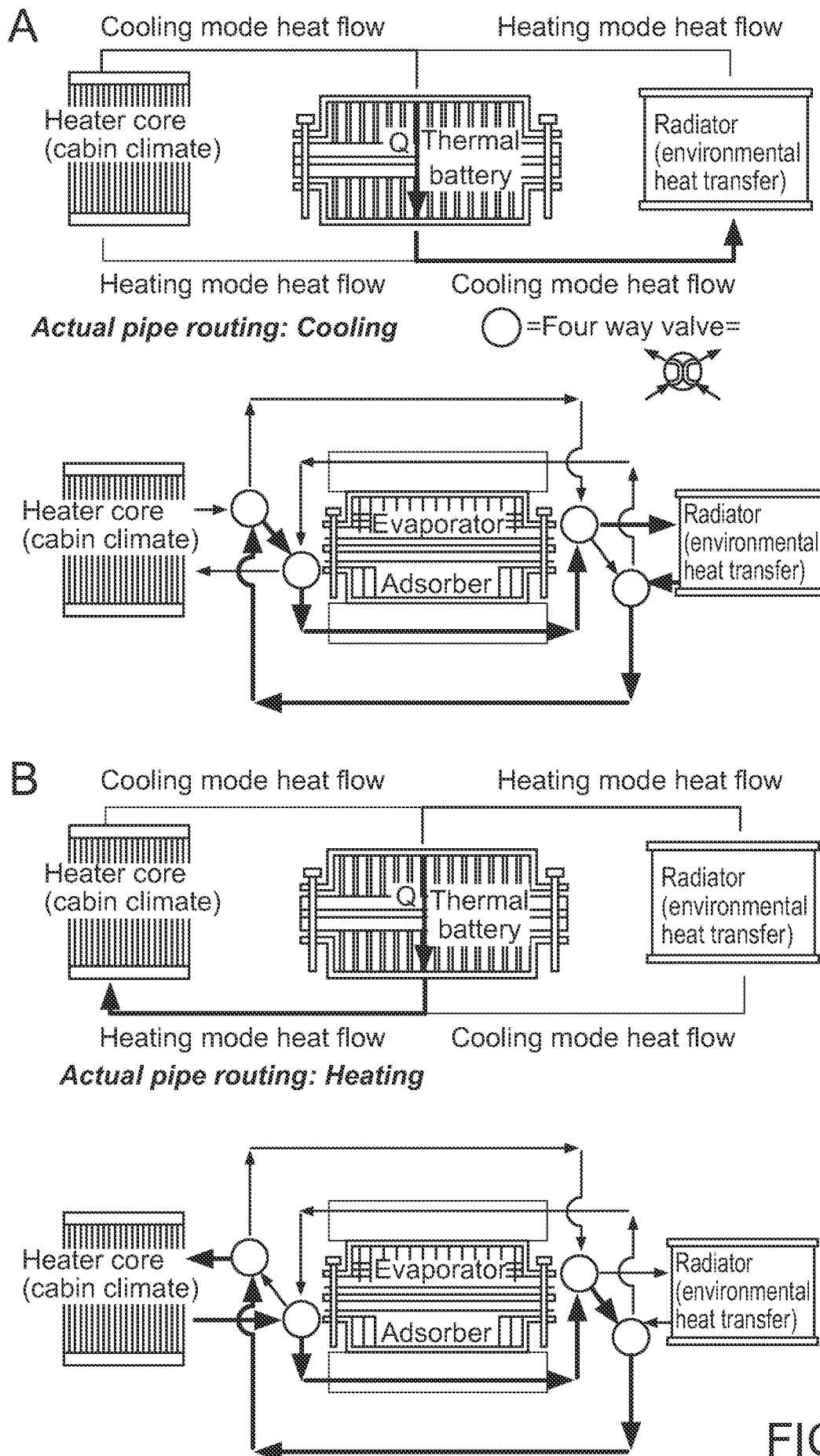


FIG. 6

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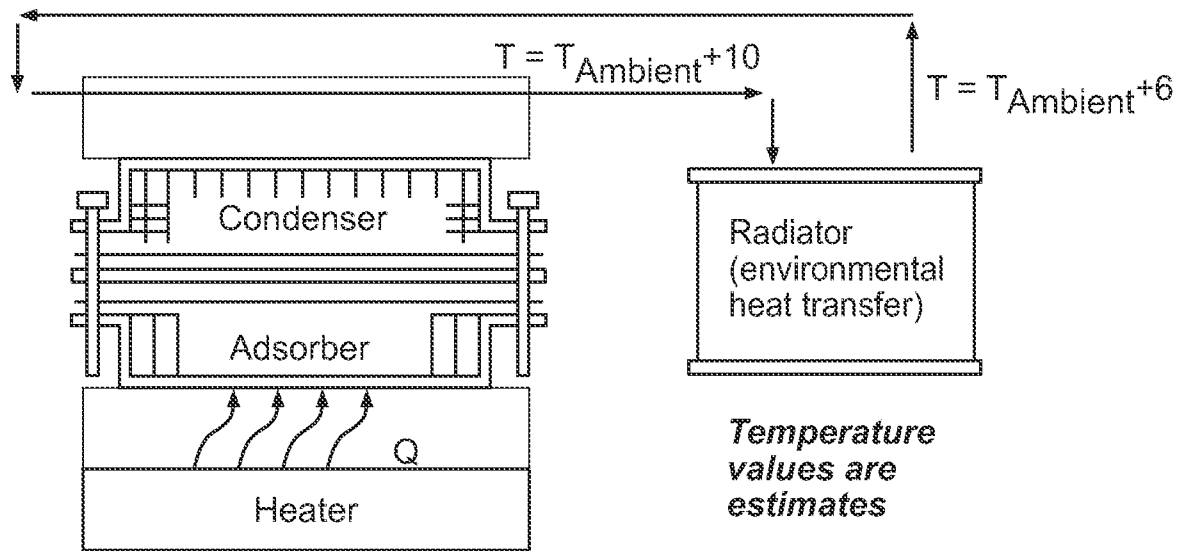


FIG. 7

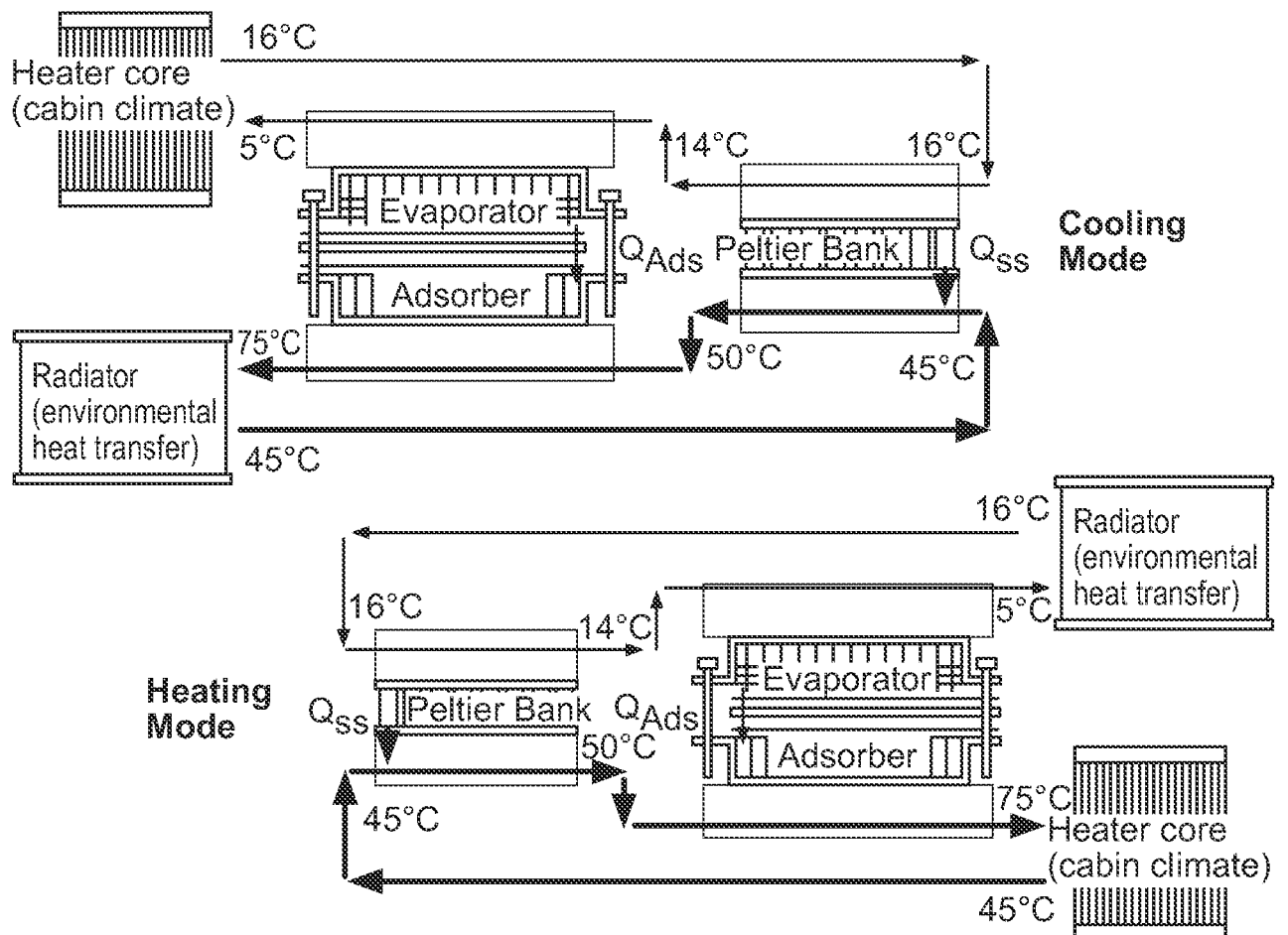


FIG. 8

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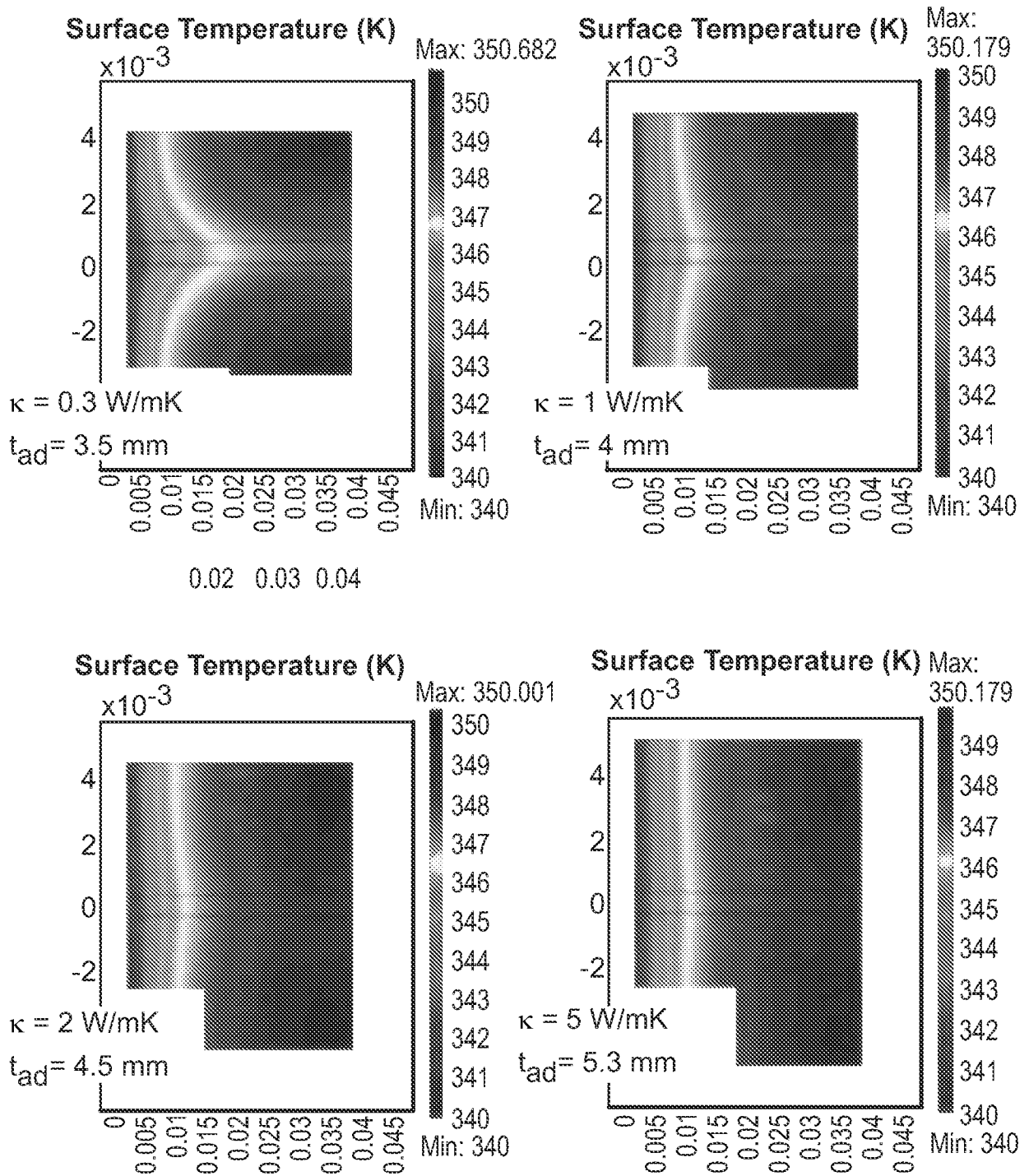


FIG. 9

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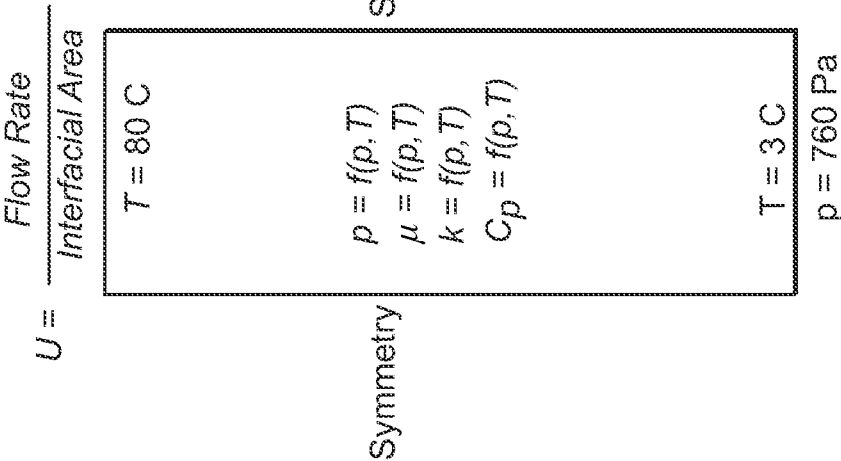


FIG. 10A

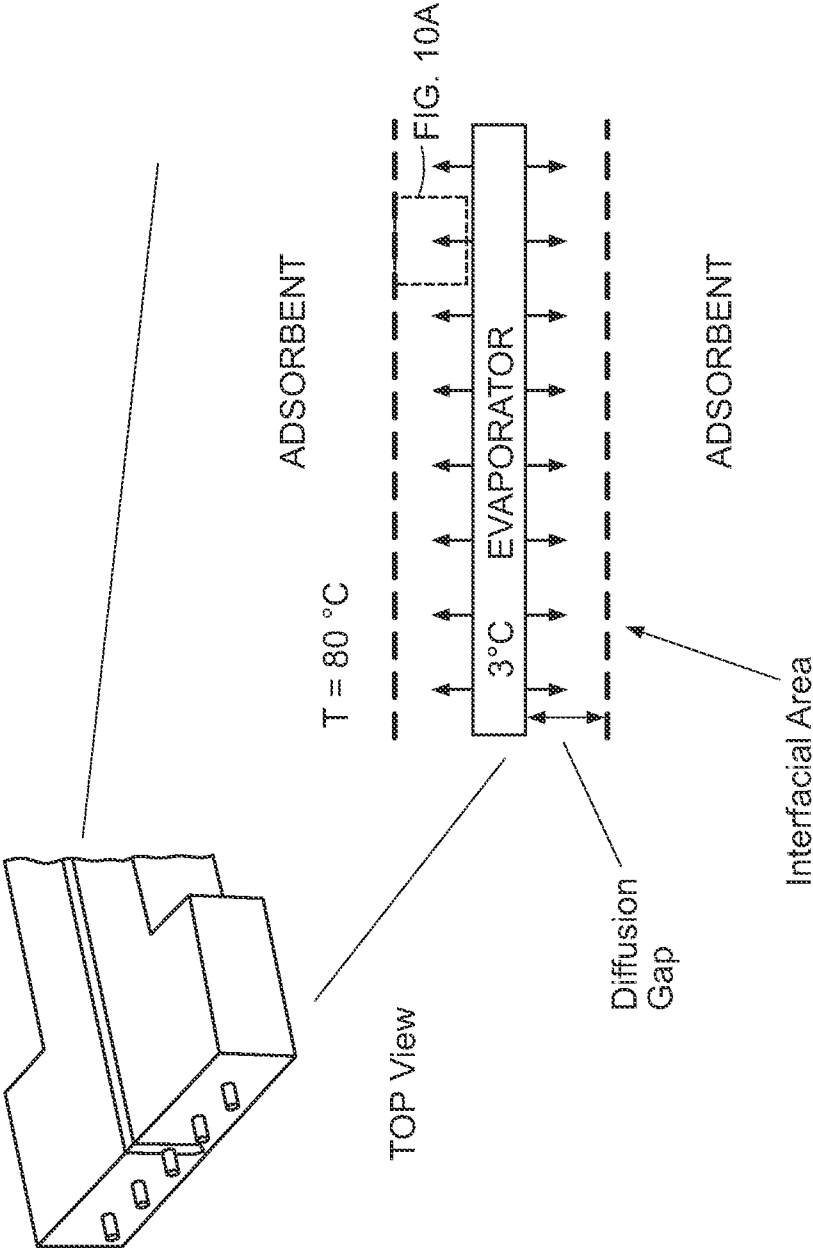


FIG. 10

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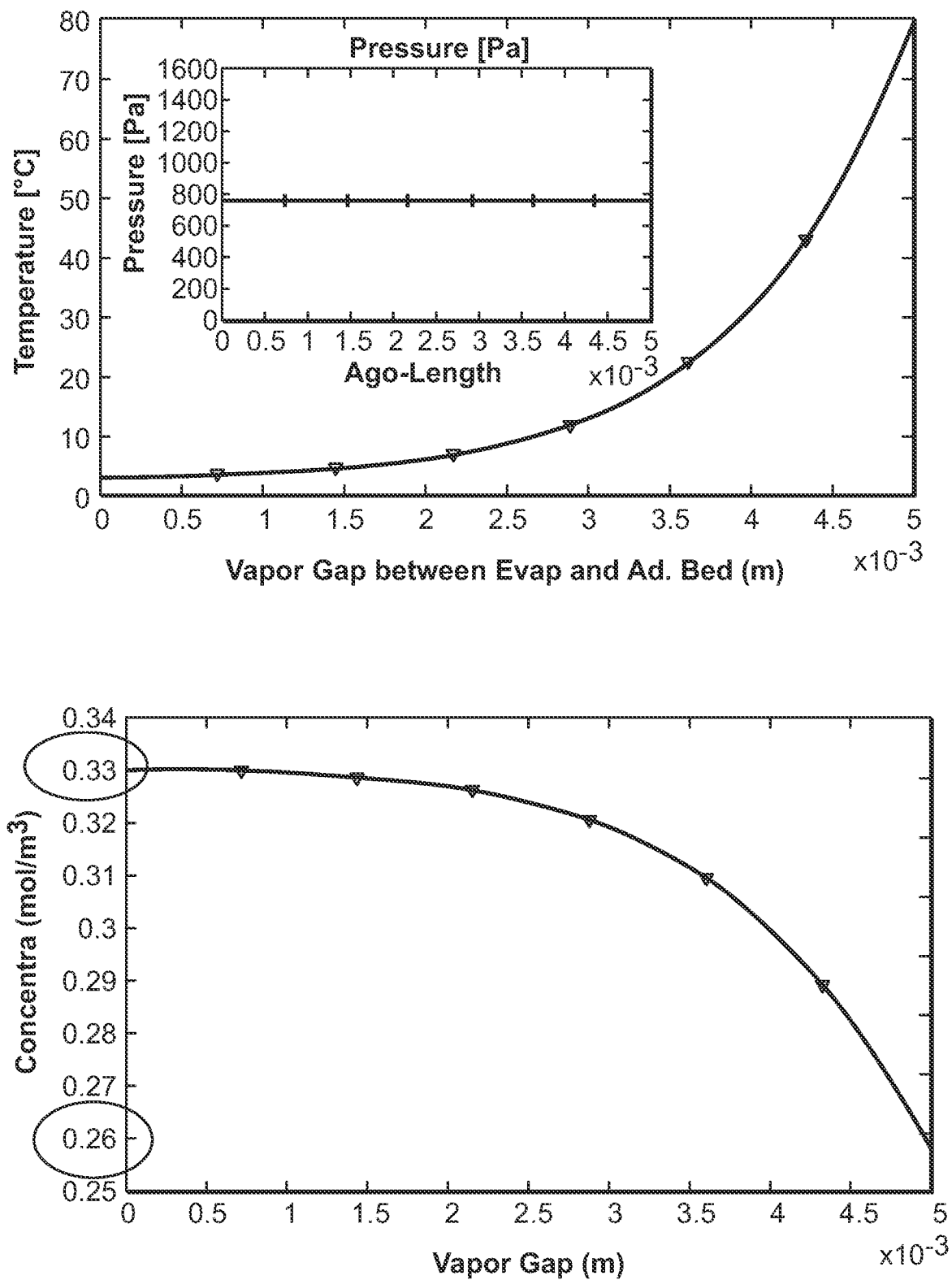


FIG. 11

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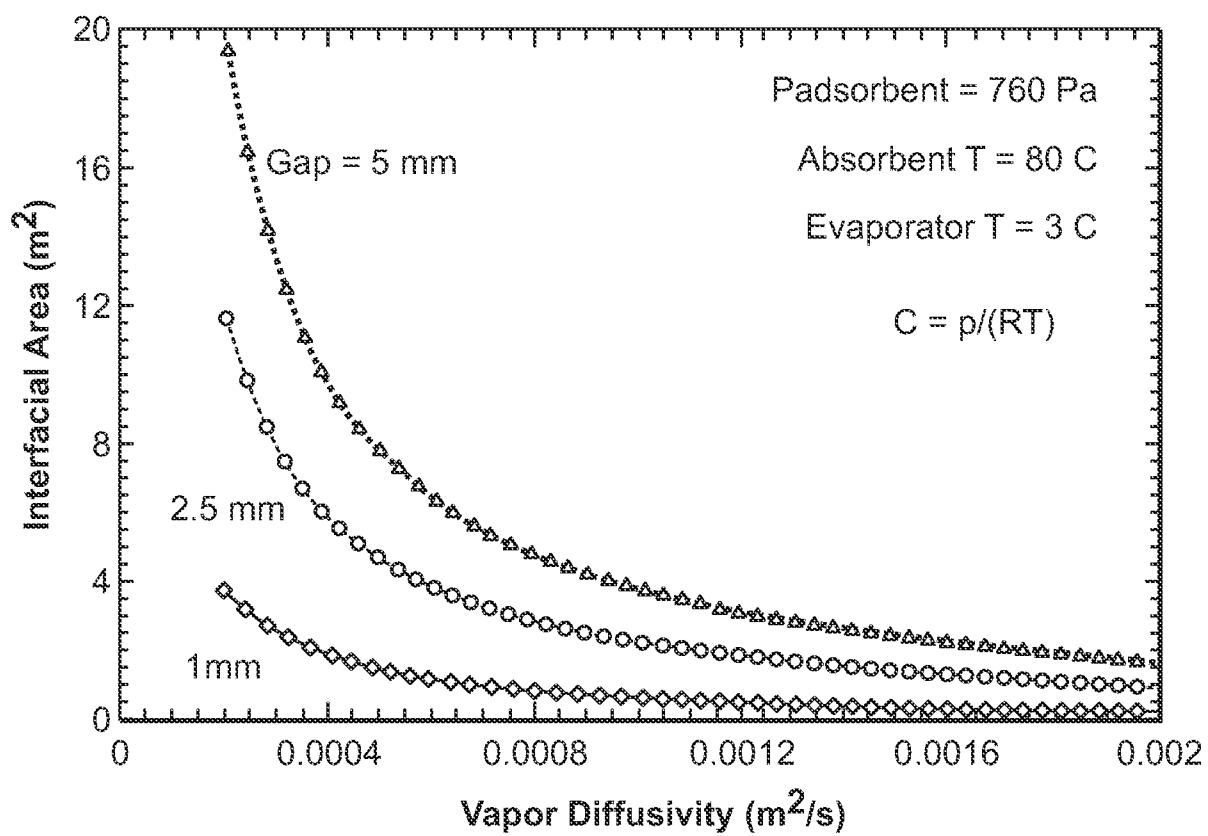


FIG. 12

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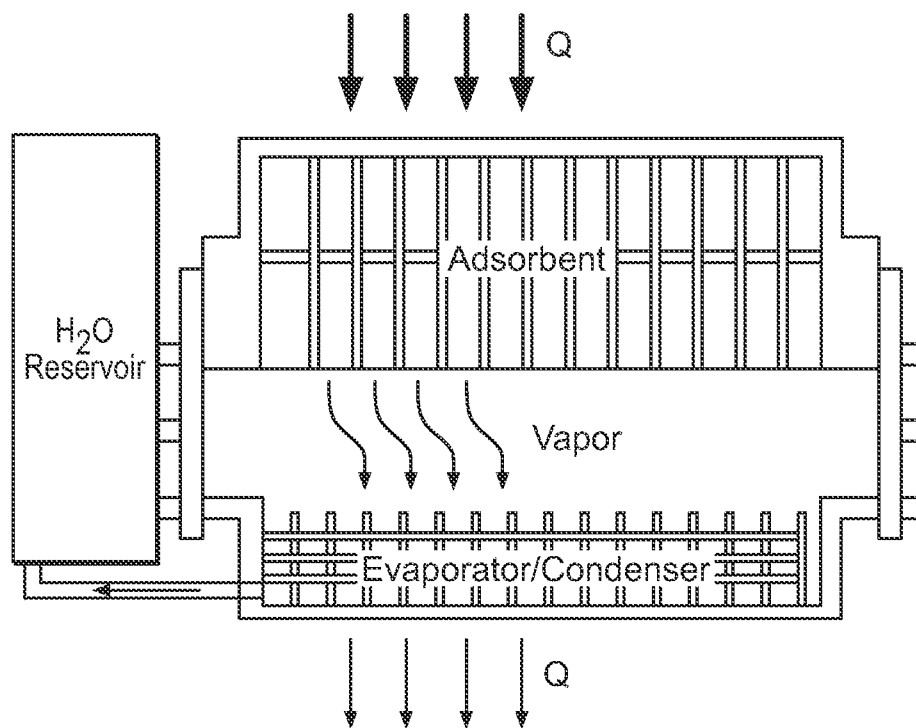
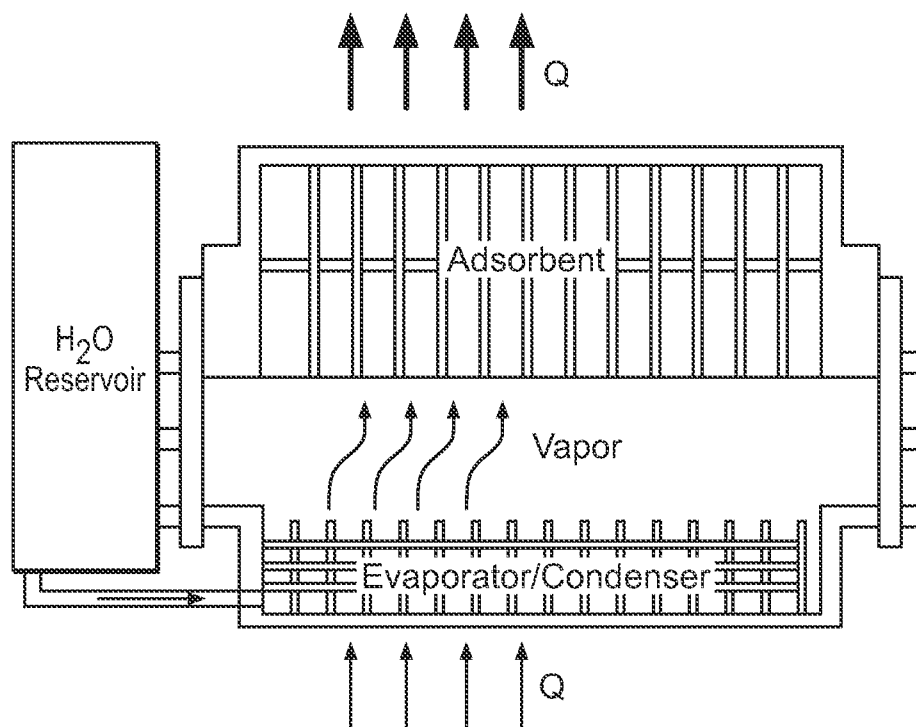
Charging the battery*Discharging the battery*

FIG. 13

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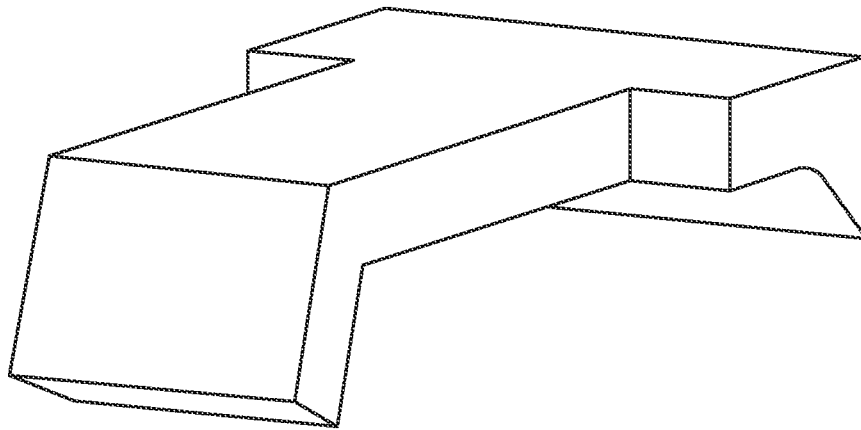


FIG. 14

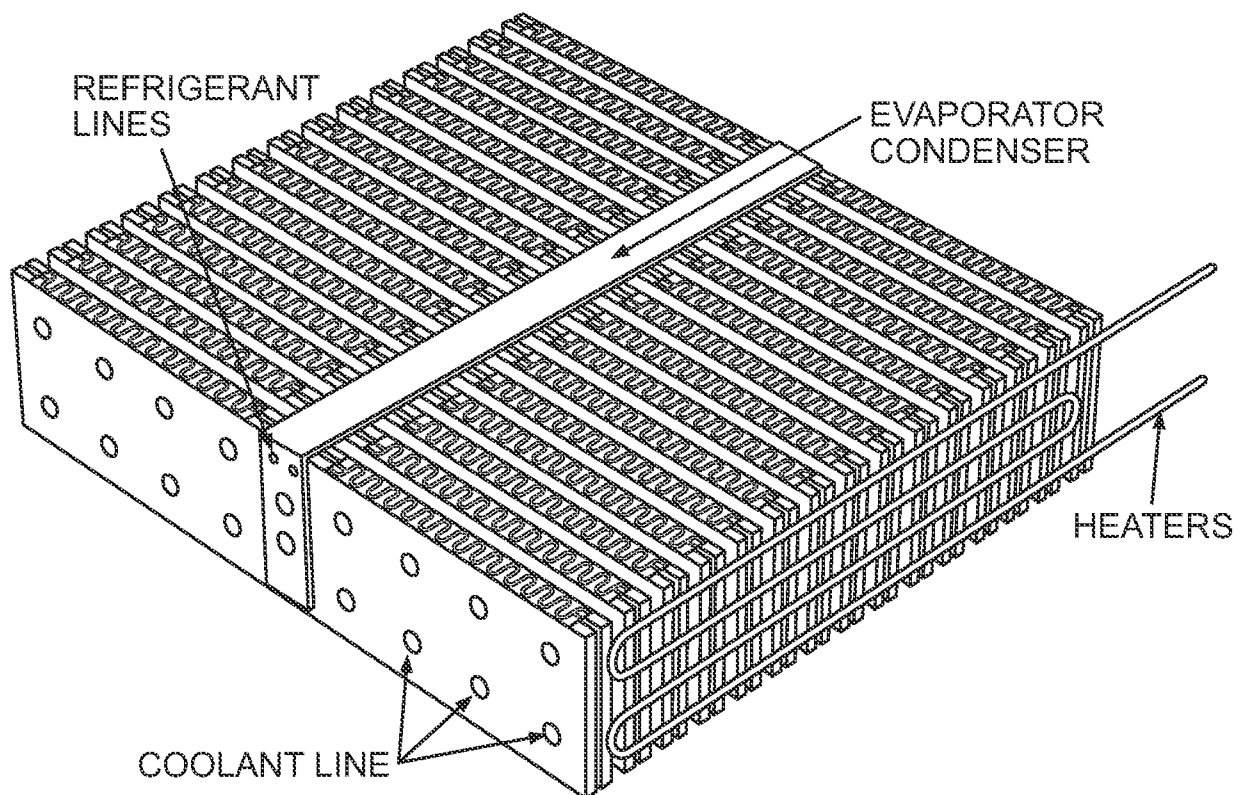


FIG. 15

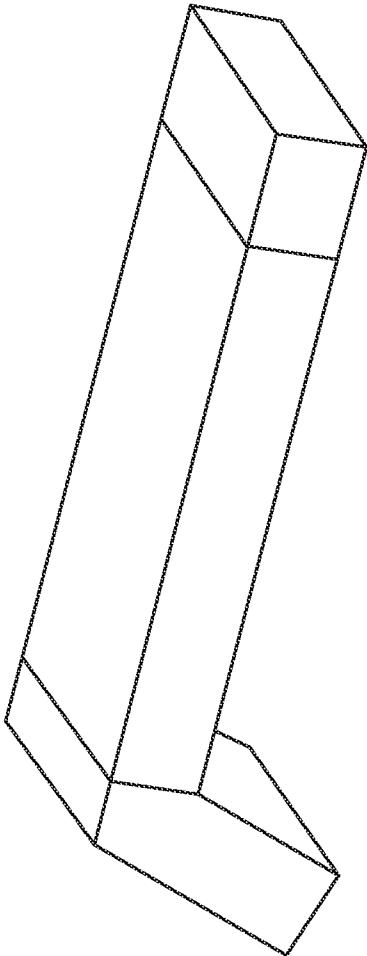


FIG. 16A

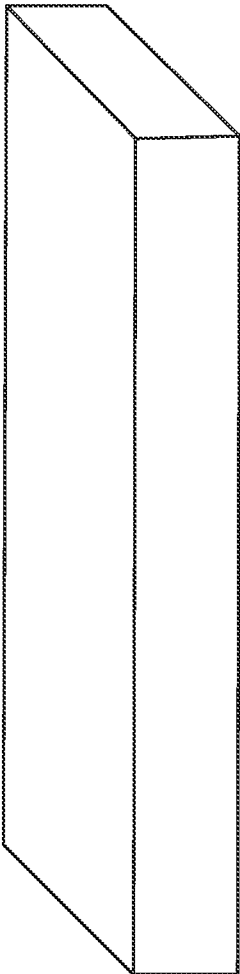


FIG. 16B

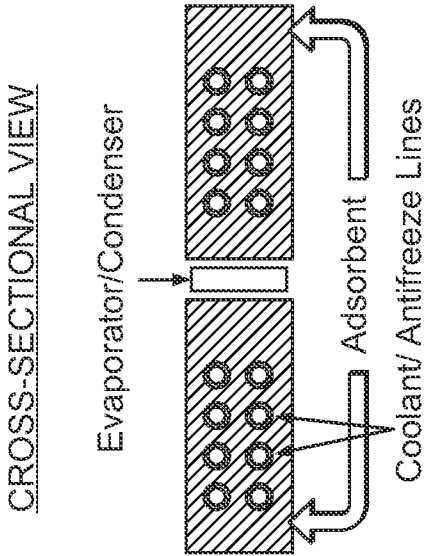


FIG. 16C

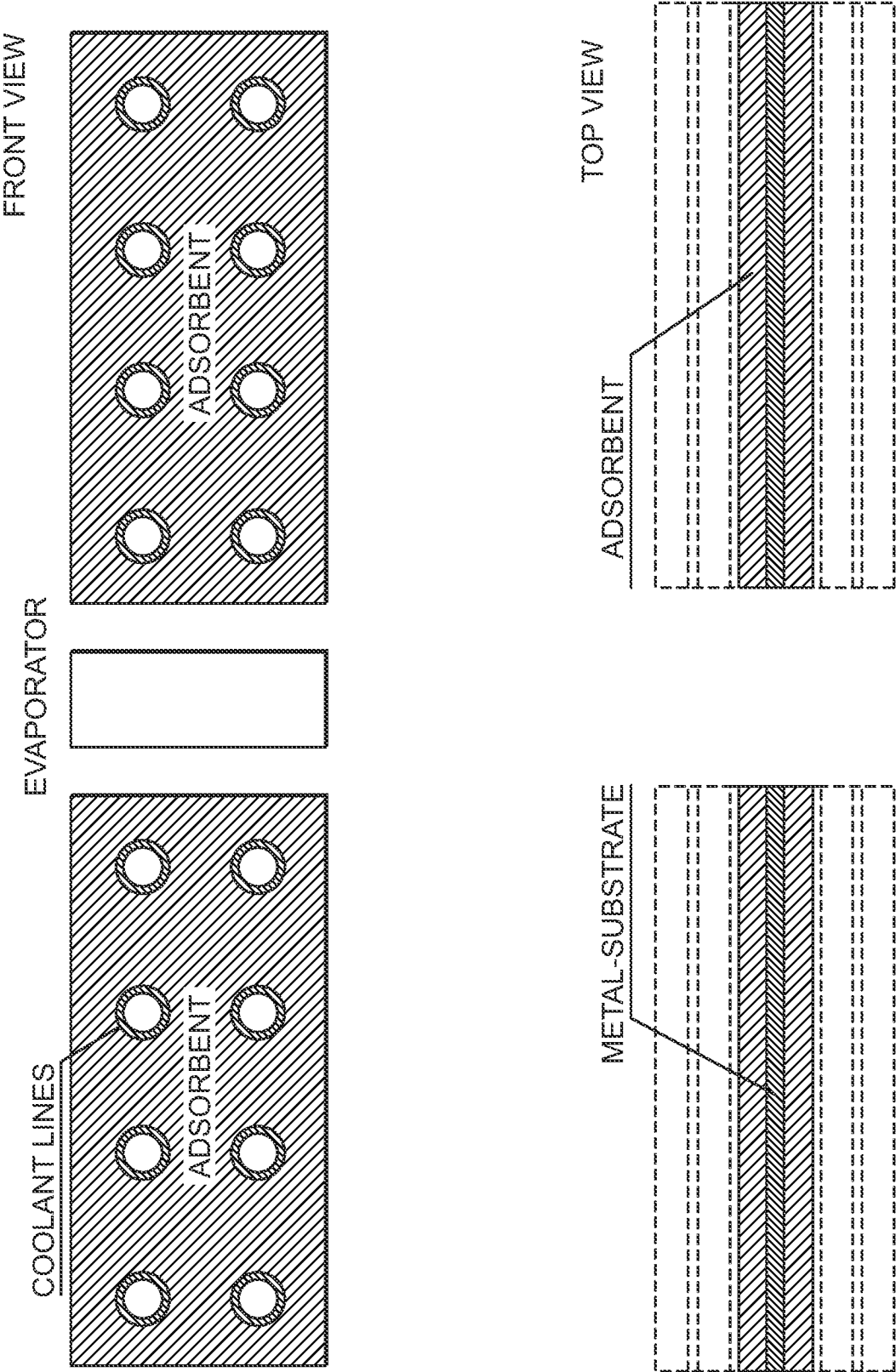


FIG. 16D

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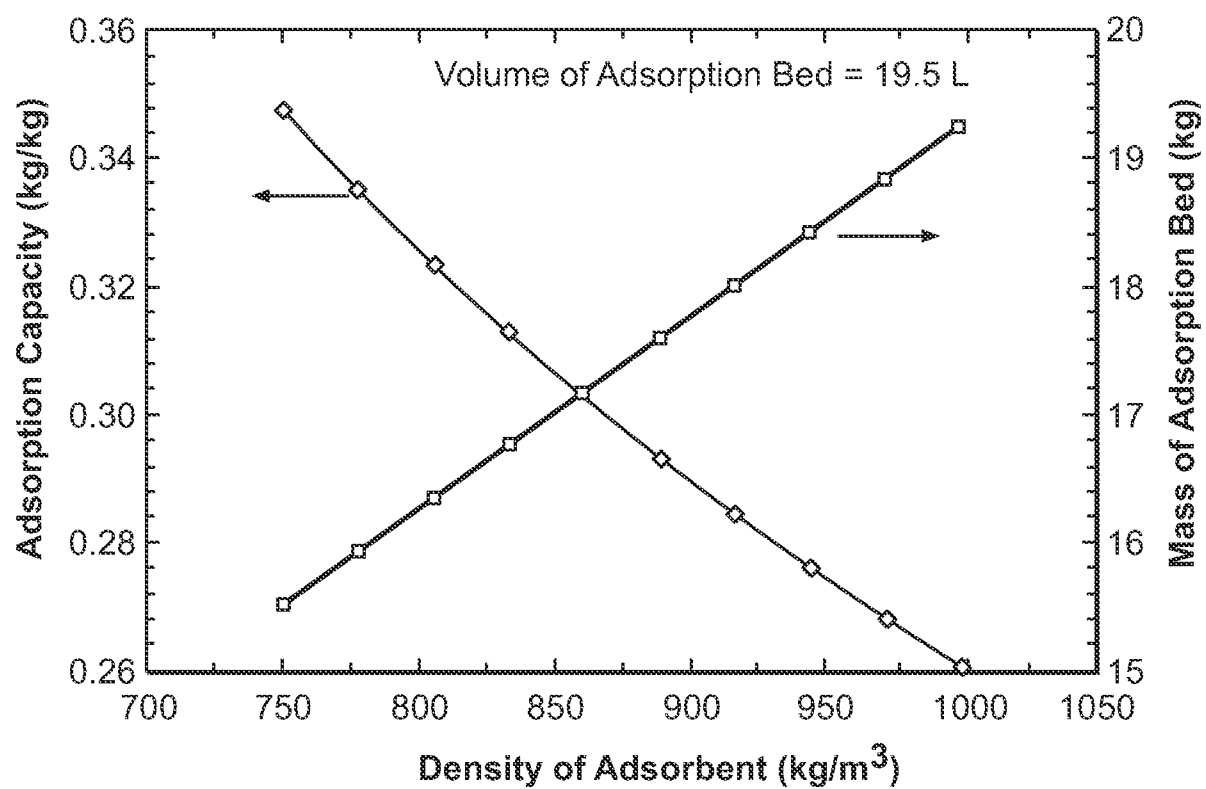


FIG. 17

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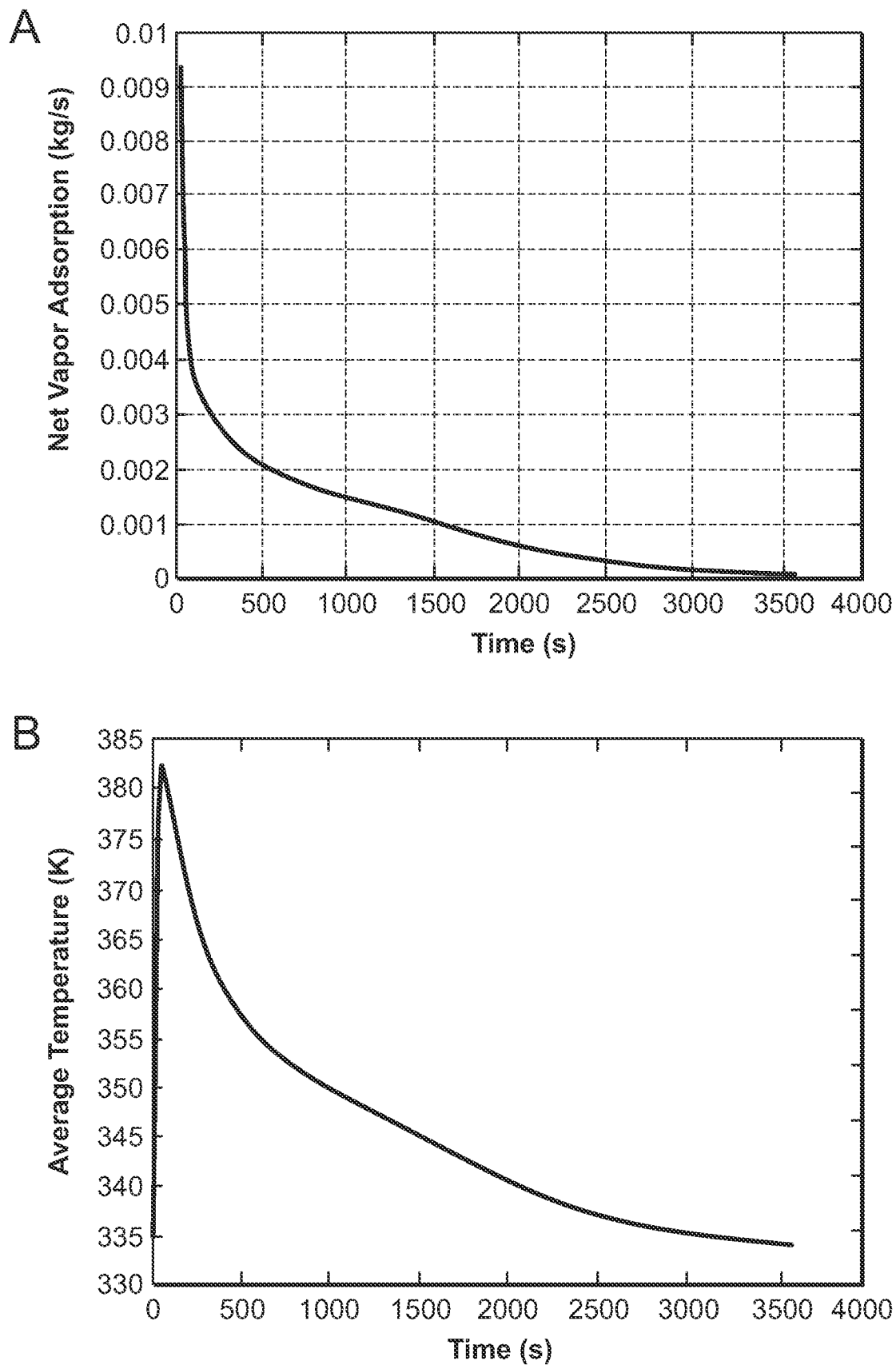


FIG. 18

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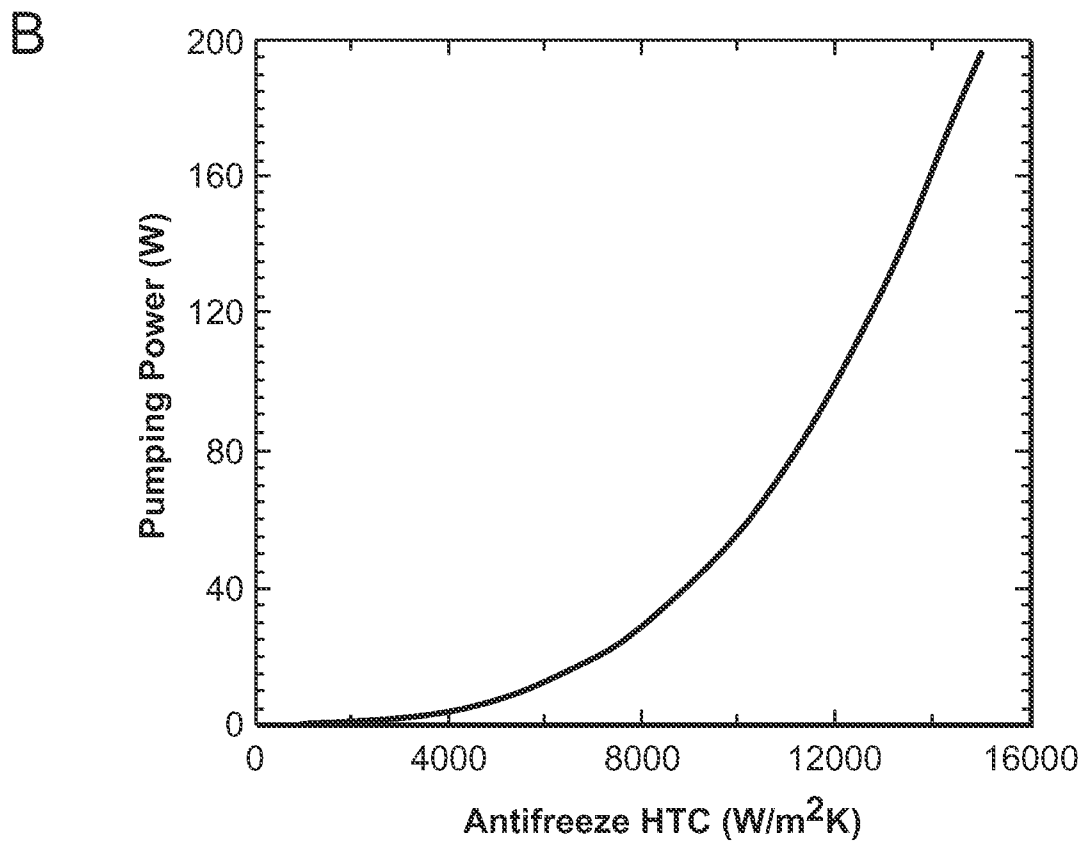
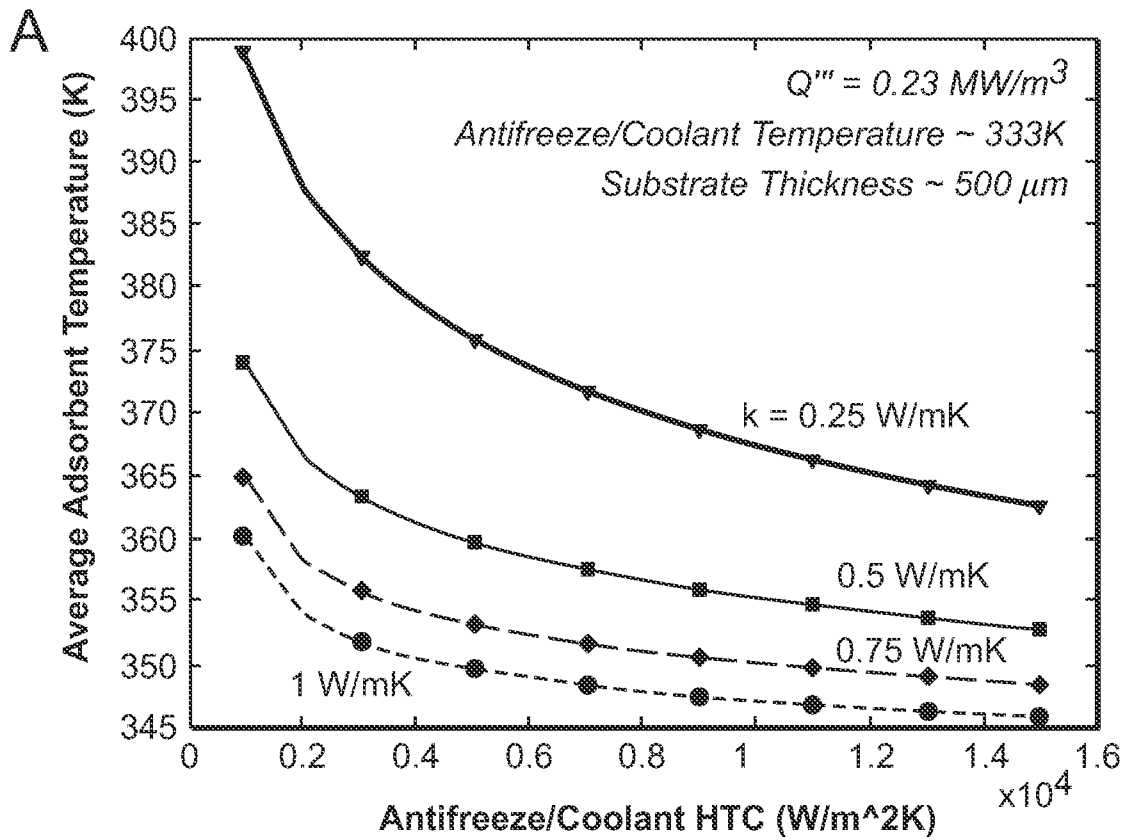


FIG. 19

SUBSTITUTE SHEET (RULE 26)

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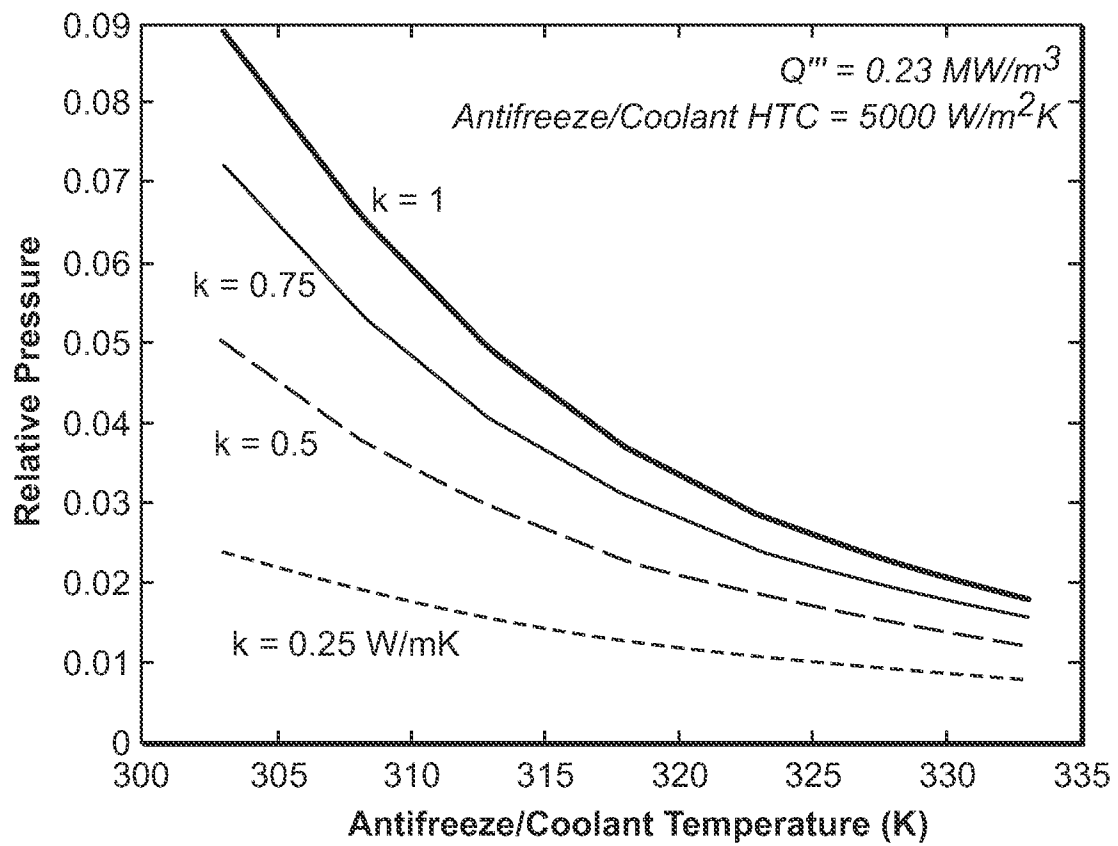


FIG. 20

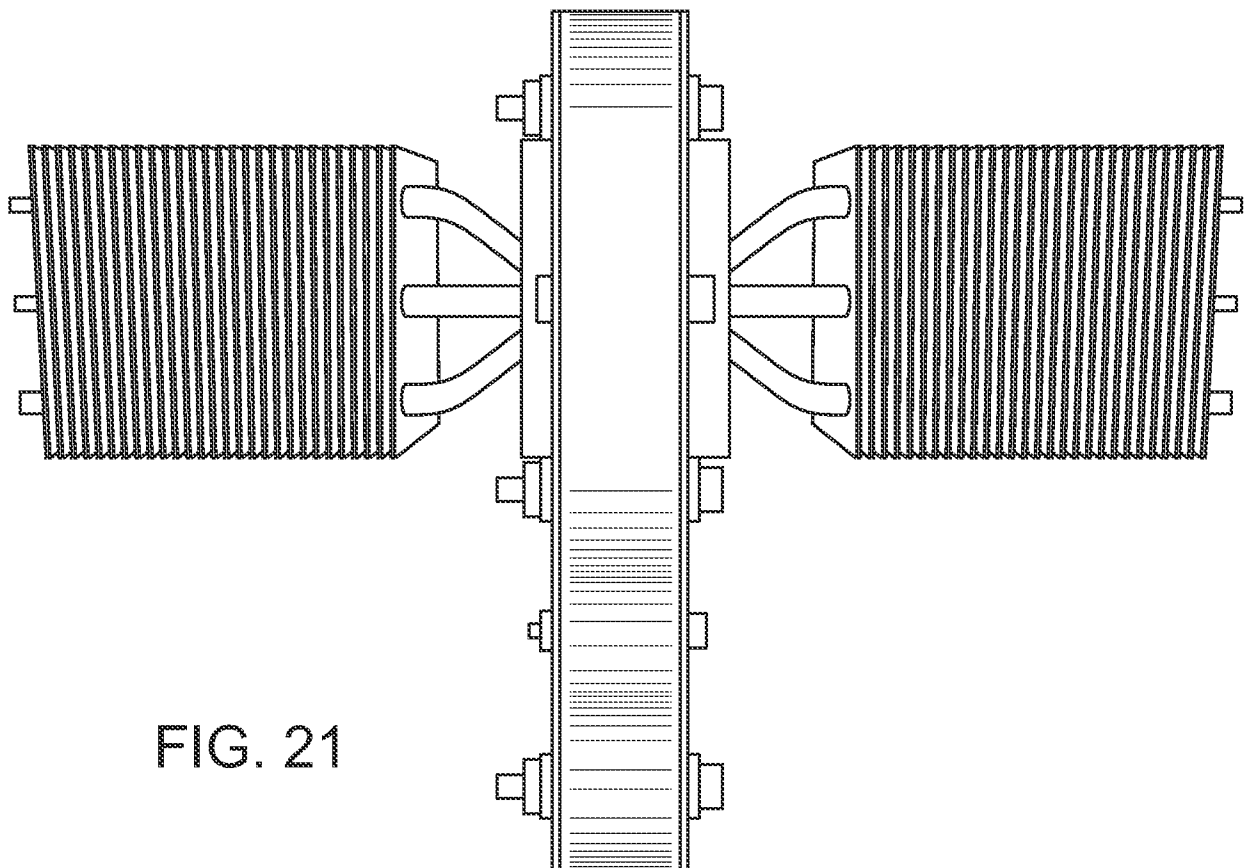


FIG. 21

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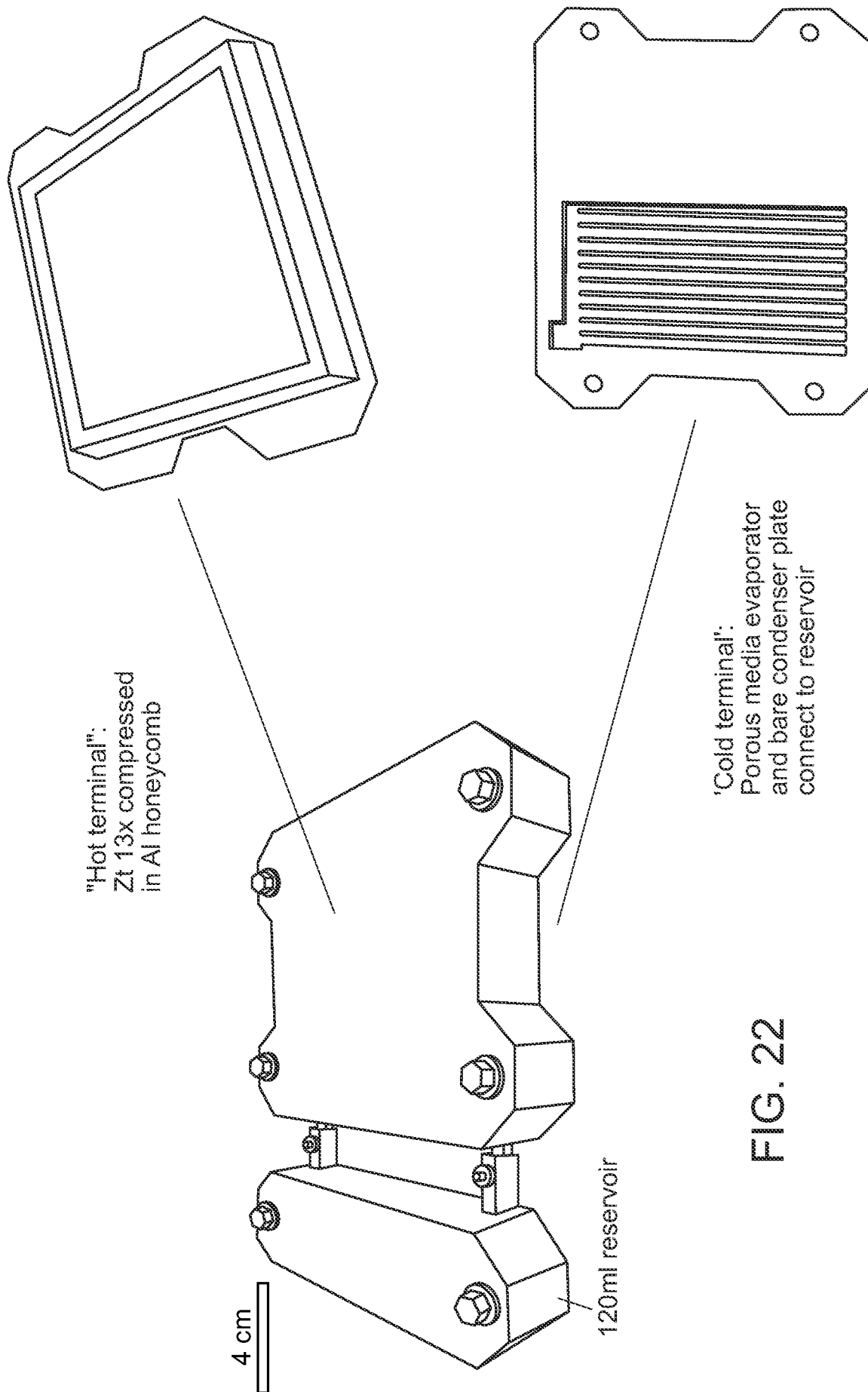


FIG. 22

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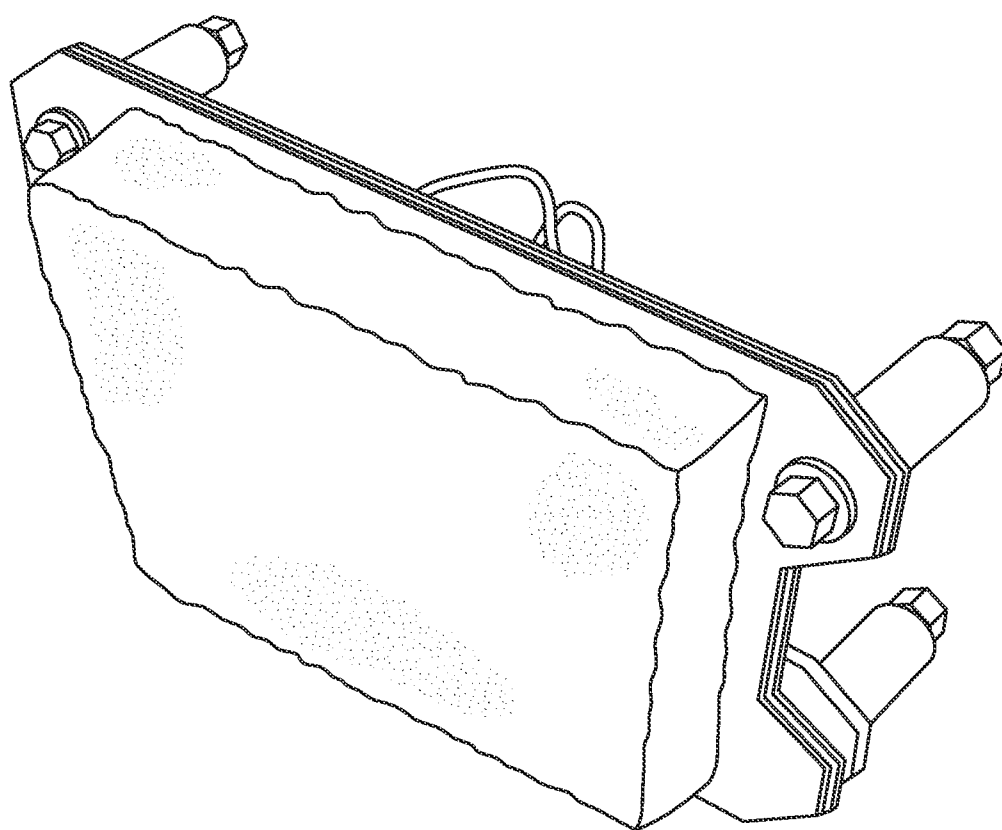


FIG. 23

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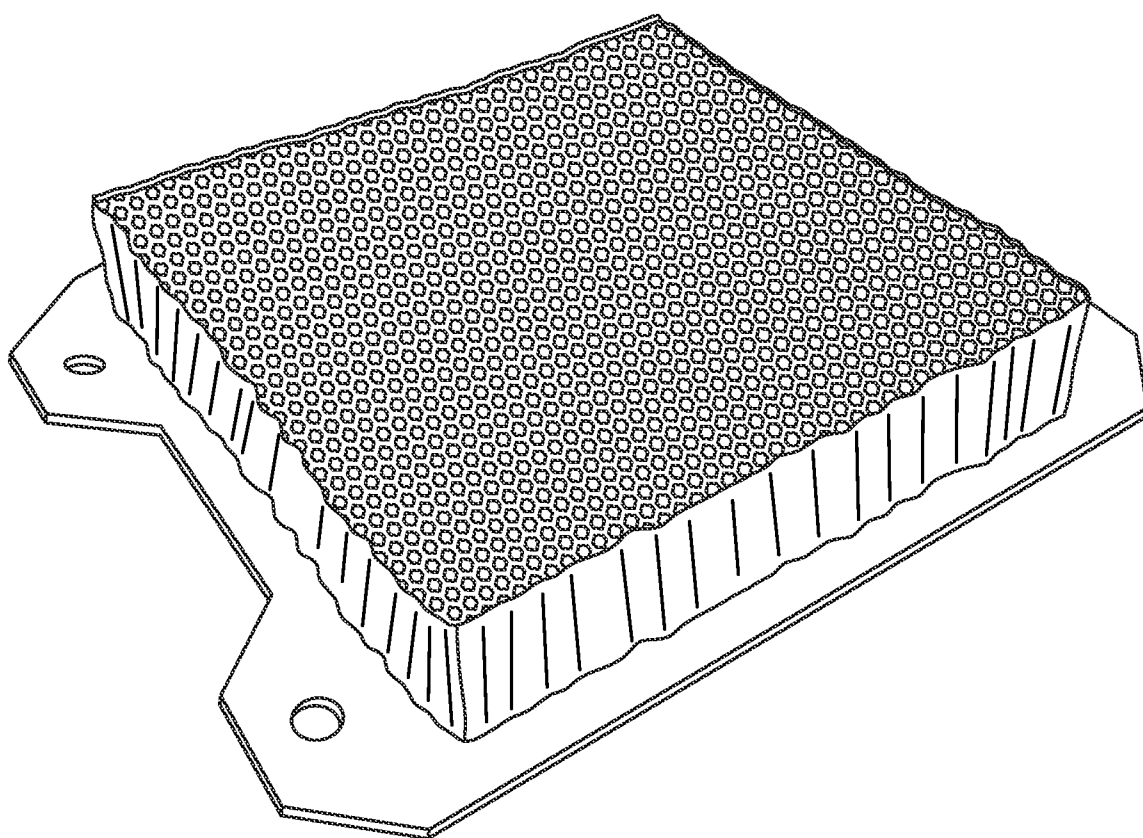


FIG. 24

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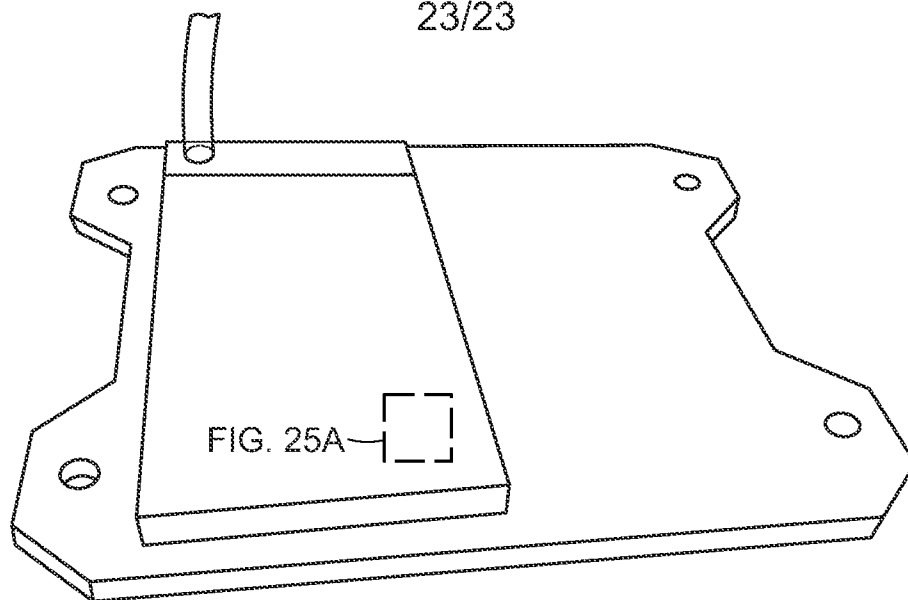
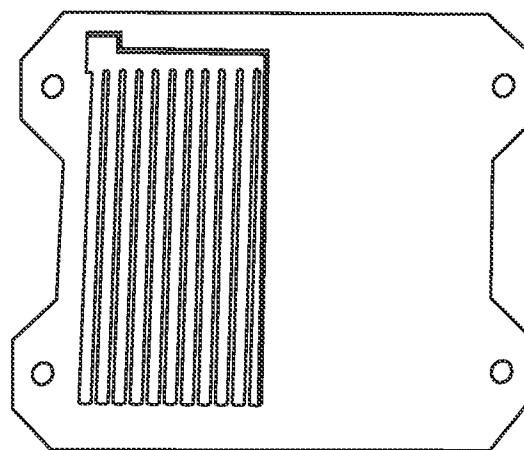
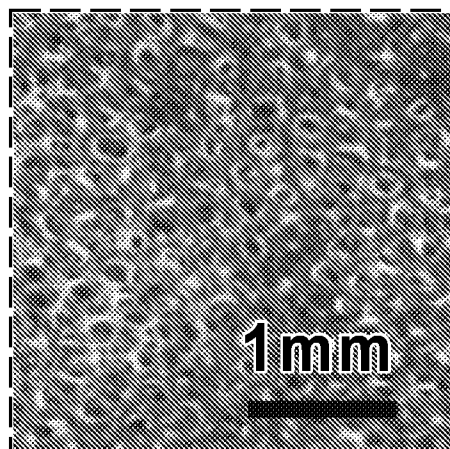


FIG. 25



Liquid direct to
minichannels
beneath porous Cu

FIG. 25A



10x Compressed 95%
porosity ~ 110 μ m pore
Cu foam

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/073549

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	F25B37/00	F25B39/00 F25B30/04 F25B17/00 F25B17/08
	F25B35/04	
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) F25B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/087682 A1 (SORTECH AG [DE]; HENNING HANS-MARTIN [DE]) 23 October 2003 (2003-10-23) page 8 - page 20; figures 1-7 -----	1-7
X	WO 2010/014878 A1 (GEORGIA TECH RES INST [US]; GARIMELLA SRINIVAS [US]; DETERMAN MATTHEW) 4 February 2010 (2010-02-04) page 16 - page 50; figures 1-24 -----	1-3
A		4-7
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search 8 April 2014		Date of mailing of the international search report 16/04/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Amous, Moez

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/073549

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03087682	A1	23-10-2003	AT 414246 T 15-11-2008
		AU 2003227620 A1 27-10-2003	
		CN 1656346 A 17-08-2005	
		DE 10217443 A1 06-11-2003	
		EP 1495272 A1 12-01-2005	
		ES 2314201 T3 16-03-2009	
		JP 4347066 B2 21-10-2009	
		JP 2005528573 A 22-09-2005	
		KR 20050016351 A 21-02-2005	
		US 2006101847 A1 18-05-2006	
		WO 03087682 A1 23-10-2003	

WO 2010014878	A1	04-02-2010	CN 102112837 A 29-06-2011
		EP 2321605 A1 18-05-2011	
		JP 2011530059 A 15-12-2011	
		KR 20110074970 A 05-07-2011	
		US 2011180235 A1 28-07-2011	
		WO 2010014878 A1 04-02-2010	
