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Metal Hydride based Cooling Systems with Hydrogen as Working Fluid – A Review

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ABSTRACT: Dry (solid) sorption systems are attractive competitors to wet (liquid) sorption systems in providing useful cold and/or useful heat. Among the dry sorption systems, those based on the absorption/desorption of hydrogen in/from metal alloys reveal advantageous features, and this has stirred up the interest of researchers already since the 1970s. In recent years, metal hydrides have attracted attention as hydrogen storage materials. These can also be used for construction of a variety of thermally driven sorption cooling systems. In this paper, the operating principles and performance of various configurations of metal hydride based cooling machines; together with the materials characteristics relevant to efficient operation of such devices are discussed. In this paper, the research and development work on metal hydride based heating and cooling systems is reviewed which has been published in the last three decades. Emphasis is given primarily to cooling/air-conditioning. Possible ways of improving the coefficient of performance and specific cooling capacity are discussed. The objectives are to provide the fundamental understanding of metal hydride based heating and cooling systems.

Keywords: Metal Hydride, Cooling system, Willers and Groll.M.

I. INTRODUCTION

While the hydrogen absorption-desorption characteristics are used for hydrogen storage, compression and purification, the reaction enthalpy changes may be applied in thermal energy storage and heat pumps. Detailed reviews of the various aspects of metal hydride based thermodynamic machines are available in references. The simple metal hydride single-stage heat pump shown in Fig.1 consists of two reactors filled with different materials A and B between which hydrogen is cyclically exchanged. The machine is operated at three temperature levels (TD>TM>TC) and two pressure levels (PH>PL). It is driven by heat input to A at the high temperature TD, thereby desorbing hydrogen. Hydrogen flows to metal B which absorbs it forming a hydride and releasing the absorption enthalpy at a medium temperature level TM (first half cycle). In the second half cycle, there is heat input to hydride B at a low temperature TC, which is the cooling load. This heat is upgraded to a higher temperature level TM by desorption at B. Then hydrogen flows to A, where it is absorbed releasing absorption enthalpy at TM. Between the two half cycles there are transition periods, where the two reactors have to be sensibly cooled or heated. The sensible heating causes thermal losses which can be compensated by internal heat and mass recovery between respective reactors. In the case of heat pump in Fig.1 there is a quasi-continuous heat output due to the cyclic operation of the machine. In case of a refrigerator (TC<TA, TM≈TA) there is only one cold generating half cycle. The same holds for the thermodynamically reversed heat pump, the heat transformer; in which there is heat input at medium temperature in each half cycle, but heat output at high temperature only in one half cycle. In the latter two cases quasi-continuous cold/heat output can be achieved by operating two pairs of reactors in parallel with a phase shift of a half cycle.

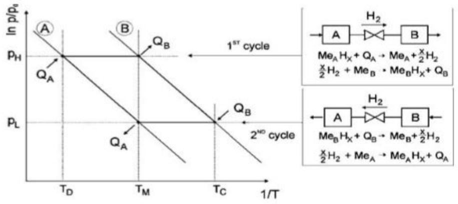


Fig. 1. Operating principle of a single stage metal hydride heat pump.

II. DIFFERENT SORPTION COOLING SYSTEM CONFIGURATIONS

Theoretically, it is possible to develop a large number of different schemes for sorption cooling systems. However, practical considerations like pressure and temperature levels, internal heat and mass exchange area, cost and properties of the working fluids limit the number of practically feasible schemes. Some typical configurations are described here.

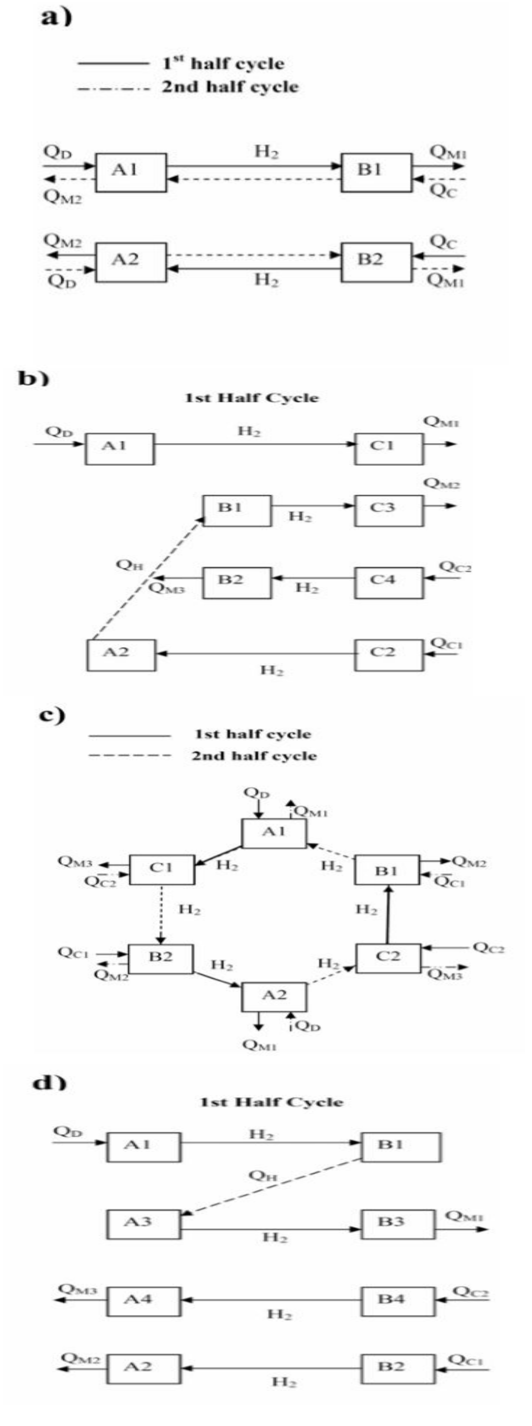


Fig. 2. Different Sorption Cooling System Configuration

A. Single-stage/single-effect system (Fig.2a)

This comprises two pairs of reactors with metal hydrides A and B. In each pair, A and B are coupled on the hydrogen side. One pair is at high pressure (A1, B1), the other is at low pressure (A2, B2). There is a heat source at temperature TD, a heat sink at temperature TM (useful heat), and a low temperature heat source at TC (useful cold). In the first half-cycle A1 is desorbed at high pressure by the driving heat QD at TD. The coupled hydride B1 absorbs the released hydrogen and the absorption heat QM1 is released at temperature TM. Simultaneously hydride B2 is desorbed at low pressure by the useful cold QC at temperature TC. The desorbed hydrogen is absorbed by A2 and the absorption heat QM2 is released as useful heat at TM. In the second half-cycle, the driving heat QD is applied to the reactor containing A2 that now desorbs hydrogen at high pressure.

The hydrogen flows to the reactor containing B2, and the heat QM1 is released at temperature TM. Simultaneously B1 is desorbed at low pressure by applying the useful cold QC. The hydrogen flows to A1 generating the heat QM2. During each half cycle useful heat is produced twice and useful cold once by applying the driving heat once. Thus, by operating two pairs of reactors in parallel one obtains a quasicontinuous cold output.

The heating up followed by cooling down of the thermal masses of the reaction beds significantly reduces the system performance. This can be minimized by internal heat recovery which becomes the more important the higher the temperature lift of one hydride is. In practice a heat recovery of about 40% is possible. Cooling temperatures of 10°C to -50°C can be obtained with the single stage system. In general the driving temperature can be from 90 to 130°C. Only in the case of very low cooling temperatures, it should be more than 200°C. Then the effects of thermal masses become more important.

B. Single-stage/double-effect system (Fig.2b)

This requires three different metal hydrides (A, B, C) in eight reactors (A1, A2, B1, B2, C1, C2, C3, C4) and four different temperature levels. In the first half-cycle, A1 is desorbed by the driving heat input at temperature TD, while the coupled C1 produces heat at temperature TM. At the same time, C2 takes up desorption heat (cold) at low temperature TC, while the released hydrogen is taken up by A2 which releases heat at temperature TH. This heat is used to desorb B1 at TH, which is coupled to C3 which in turn absorbs at TM. C4 takes up desorption heat (cold) at low temperature TC, while the coupled B2 absorbs at TM.

C. Double-stage/double-effect system (Fig.2c)

This employs three different metal hydrides (A, B, C). In a special star scheme design there are six interconnected reactors (A1, A2, B1, B2, C1, C2). Each hydride is connected with the other two hydrides on the hydrogen side. All reactors are simultaneously in operation.

The star-scheme operates in two half-cycles and allows a continuous cold and heat generation. Three different temperature levels are at least necessary: TD as heat source (driving heat), TM as heat sink (useful heat) and TC as low temperature heat source (useful cold). In the first half cycle A1 is desorbed by the driving heat QD at temperature TD. It is coupled on the hydrogen side with C1 where the absorption heat QM3 at TM is released. B2 is desorbed by the heat QC1 (useful cold) at temperature TC. It is coupled on the hydrogen side with A2where the absorption heat QM1 at temperature TM is released. C2 is desorbed by the heat input QC2 at TC. It is coupled on the hydrogen side with hydride B1 where the absorption heat QM2 at TM is released. After the first half-cycle an internal heat recovery between A1 and A2, between B1 and B2 and between C1 and C2 takes place. Now the hydrogen valves and fluid valves are interchanged and the second half-cycle takes effect as follows: A2 is desorbed by QD at TD and C2 absorbs QM3 at TM; B1 is desorbed by QC1 at TC and A1 absorbs QM1 at TM; C1 is desorbed by QC2 at TC and B2 absorbs QM2 at TM.

D. Double-effect/double-stage system (Fig.2d)

This requires two hydrides (A, B) in eight reactors (A1, A2, A3, A4, B1, B2, B3, B4). In the first half cycle reactor A1 is desorbed by QD while the coupled reactor B1 is absorbing and releasing QH. This heat is used to desorb reactor A3 which is coupled to reactor B3, releasing QM1. Meanwhile, the reactors B2 and B4 are desorbed by the useful cold QC1 and QC2 at TC and their coupled reactors A2 and A4 absorb and release QM2 and QM3. This system requires at least four different temperature levels: TD as driving heat source, TH as internal heat exchange temperature, TM as useful heat sink and TC as low temperature heat source (useful cold).

III. SELECTION OF ALLOYS

Performance of the MHHP systems are characterized by coefficient of performance (COP) and specific cooling power (SCP). These largely depend on the thermodynamic and thermo physical properties of the metal hydride pairs. In general, the alloys must have high enthalpy of formation, low specific heat, high hydrogen absorption capacity, high thermal conductivity and fast reaction kinetics. Favourable equilibrium pressure, low hysteresis and flat plateau are essential. Simple activation characteristics are desirable. Cost, easy availability and long life with repeated cycling are also important for a practical system.

Since the hydrogen absorbing materials can be just “intermetallic composites” and not necessarily be “stoichiometric alloys”, a large number of compositions have been synthesized and recommended for use in heat pumps. Lanthanum, mischmetal, zirconium, titanium and vanadium based alloys have better overall properties and hence been recommended by many investigators.

IV. HEAT AND MASS TRANSFER ASPECTS

The absorption and desorption of hydrogen in metal hydride are exothermic and endothermic respectively. Effective supply and removal of heat from the hydride bed in the reactor is crucial. Fast reaction kinetics of hydriding materials can be best utilized to result in fast desorption and absorption rates in reactors which are designed for optimum heat and mass transfer.

A. Heat and Mass Transfer in Hybrid Reactors

The hydride reactor forms the basic building block of the adsorption cooling system. As seen earlier, a minimum of two reactors are required for a single stage intermittent system. Various analytical studies have been reported on the heat and mass transfer process in a metal hydride bed starting from simple one dimensional model with conduction proposed by Ram Gopal et al. conduction with convection by Nakagawa et al., and conduction, convection together with radiation by Askri et al.. Two dimensional and three dimensional models have also been studied by Jemni et.al, Aldas et al. and Demircan et al. The author has presented many heat and mass transfer studies on the hydride reactors.

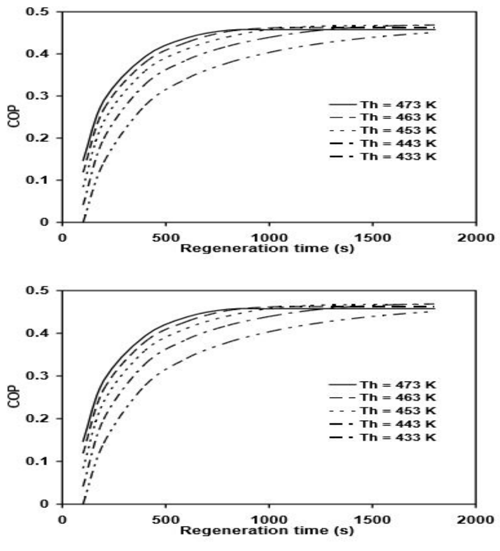
In general it has been observed that the effects of convection are important while radiation may be neglected, especially for low temperature beds encountered in refrigeration systems. Cylindrical configuration is generally preferable and two dimensional heat and mass transfer models are adequate as the variation in θ- direction is negligible. Also, the effect of bulk diffusion should be considered to accurately predict the mass transfer in the solid matrix. Recognizing the fact that the movement of hydrogen within the hydride bed and diffusion within the particles is important, a detailed CFD based two dimensional analysis has been reported by the author.

In addition to the alloy powder, the typical reactor includes the outer container, the heat transfer tubes and filters for distributing hydrogen. These add to the thermal mass of the reactor and contribute to the sensible heating / cooling losses due to the repeated cycling. Hence, these parasitic thermal masses are to be minimized by minimizing the weight of the reactor. Such a study has been recently reported by the author.

B. Performance of Hydride based Cooling Systems

Transient hydrogen transport and heat transfer between the paired reactors of a MHHP system have been studied by various authors. Lee et al. investigated the operating performance of a prototype of MHHP using $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$-$Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4}$ pair. The maximum cooling power obtained under the optimum operating conditions was about 0.15 kW/kg and the lowest cooling temperature reported was about 18°C.

They concluded that zirconium based alloy pairs yield better COPs due to their large hydrogen storage capacities and reasonably high enthalpies of formation. Similar studies have also carried out by Kang and Lee using LaNi4.7Al 0.3 – LaNi5 pair for heat pump application. The effects of various governing parameters such as, heat source temperature, cooling water temperature, convection heat transfer coefficient and chilled water temperature on system performance were extensively studied. It is observed that the COP and heating output increase with convection heat transfer coefficient, up to about 1500 W/m2K, beyond which the increase of convective heat transfer coefficient did not have significant effect. However, the rise in heat source temperature yielded increase in both the COP and heating output by about 10% for every 10°C. Ram Gopal and Srinivasa Murthy predicted the performance of a cooling system working with ZrMnFe – MmNi4.5Al0.5 pair for various operating conditions. They observed that for a bed thickness of 3 mm, an effective thermal conductivity of 4 W/mK would be an optimum value. Subsequently, they also carried out an experimental study with the same working pair of ZrMnFe – MmNi4.5Al0.5. Depending upon the operating conditions, the specific cooling rate was found to lie between 30 – 45 W/ kg of alloy and COP varied between 0.2 – 0.35. Their numerical results were compared with the experimental values and showed a reasonable agreement. However, this model is suitable mainly for thin beds and reactors of low thermal mass.



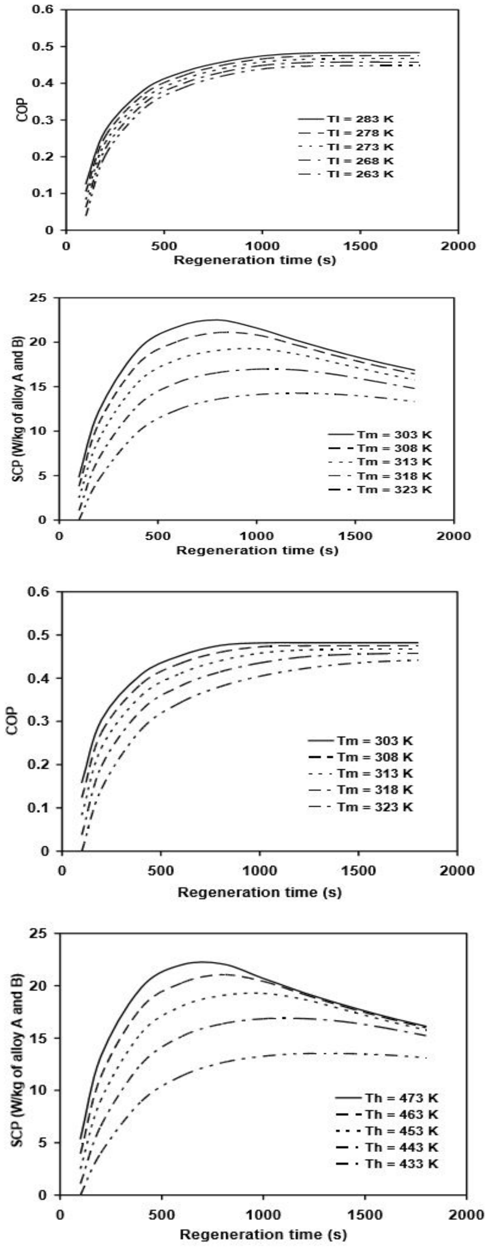
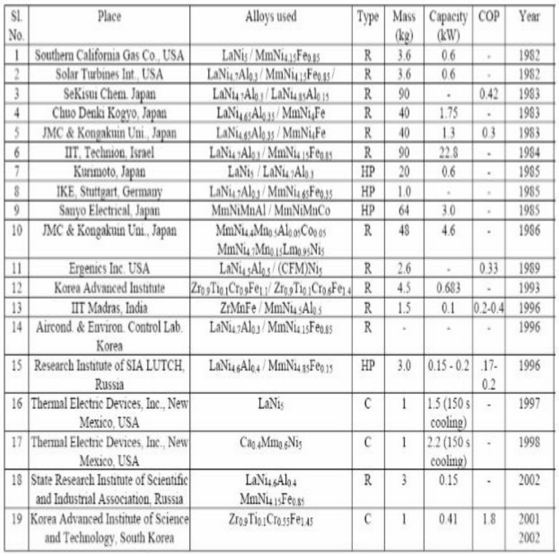


Fig. 3. Simulated Performance of a Metal Hydride Cooling System.

Recently, Ajay et al simulated a cooling module filled with two different metal hydrides LaNi4.7Al0.3 and MmNi4.15Fe0.85. Typical results are presented in Fig. 3. Table 1 gives comprehensive information on the various laboratory models tested.

Table 1. Status of Metal Hydride Based Cooling System Development around the World.



Sl. No.	Place	Alloys used	Type	Mass (kg)	Capacity (kW)	COP	Year
1	Southern California Gas Co., USA	$LaNi_5$ / $MmNi_{4.15}Fe_{0.85}$	R	3.6	0.6	-	1982
2	Solar Turbines Int., USA	$LaNi_{4.7}Al_{0.3}$ / $MmNi_{4.15}Fe_{0.85}$ /	R	3.6	0.6	-	1982
3	SeKisui Chem. Japan	$LaNi_{4.7}Al_{0.3}$ / $LaNi_{4.85}Al_{0.15}$	R	90	-	0.42	1983
4	Chuo Denki Kogyo, Japan	$LaNi_{4.65}Al_{0.35}$ / $MmNi_4Fe$	R	40	1.75	-	1983
5	JMC & Kongakuin Uni., Japan	$LaNi_{4.65}Al_{0.35}$ / $MmNi_4Fe$	R	40	1.3	0.3	1983
6	IIT, Technion, Israel	$LaNi_{4.7}Al_{0.3}$ / $MmNi_{4.15}Fe_{0.85}$	R	90	22.8	-	1984
7	Kurimoto, Japan	$LaNi_5$ / $LaNi_{4.7}Al_{0.3}$	HP	20	0.6	-	1985
8	IKE, Stuttgart, Germany	$LaNi_{4.7}Al_{0.3}$ / $MmNi_{4.65}Fe_{0.35}$	HP	1.0	-	-	1985
9	Sanyo Electrical, Japan	MmNiMnAl / MmNiMnCo	HP	64	3.0	-	1985
10	JMC & Kongakuin Uni., Japan	$MmNi_{4.4}Mn_{0.5}Al_{0.05}Co_{0.05}$ $MmNi_{4.7}Mn_{0.15}Lm_{0.95}Ni_5$	R	48	4.6	-	1986
11	Ergenics Inc. USA	$LaNi_{4.5}Al_{0.5}$ / $(CFM)Ni_5$	R	2.6	-	0.33	1989
12	Korea Advanced Institute	$Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$/ $Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4}$	R	4.5	0.683	-	1993
13	IIT Madras, India	ZrMnFe / $MmNi_{4.5}Al_{0.5}$	R	1.5	0.1	0.2-0.4	1996
14	Aircond. & Environ. Control Lab. Korea	$LaNi_{4.7}Al_{0.3}$ / $MmNi_{4.15}Fe_{0.85}$	R	-	-	-	1996
15	Research Institute of SIA LUTCH, Russia	$LaNi_{4.6}Al_{0.4}$ / $MmNi_{4.85}Fe_{0.15}$	HP	3.0	0.15 - 0.2	.17-0.2	1996
16	Thermal Electric Devices, Inc., New Mexico, USA	$LaNi_5$	C	1	1.5 (150 s cooling)	-	1997
17	Thermal Electric Devices, Inc., New Mexico, USA	$Ca_{0.4}Mm_{0.6}Ni_5$	C	1	2.2 (150 s cooling)	-	1998
18	State Research Institute of Scientific and Industrial Association, Russia	$LaNi_{4.6}Al_{0.4}$ $MmNi_{4.15}Fe_{0.85}$	R	3	0.15	-	2002
19	Korea Advanced Institute of Science and Technology, South Korea	$Zr_{0.9}Ti_{0.1}Cr_{0.55}Fe_{1.45}$	C	1	0.41	1.8	2001 2002

(R=Refrigerator, HP=Heat Pump, C=Compressor Driven System)

V. HEAT AND MASS TRANSFER

The conventional wet vapour absorption systems always have a solution heat exchanger to recover the heat. Though to a lesser extent, such heat would be available in the case of MHHP systems, but is difficult to recover since the "absorbent" in this case is solid and does not flow. Kevin et al. have made extensive studies to recover this heat by way of mass and then heat recovery and concluded that by recovering mass and heat, the COP could be increased by about 10 – 15%. Excess heat is recovered by transferring the heat from the hot high temperature reactor after itsdesorption process to warm high temperature reactor, which just finished its absorption process. Typical results for a cooling system with Zr0.9Ti 0.1CrFe and Zr0.7Ti0.3CrFe as high temperature alloy and low temperature alloy respectively are shown in Fig.4.

The heat transfer process can be made more efficient by thermal wave scheme reported by Willers et al. and Willers and Groll. They presented a comparative performance study of a metal hydride heat pump with single-stage, double-stage and the novel multi-hydride thermal-wave concept. Using high performance reaction beds, cycle time of about 5 -10 min was obtained. Correspondingly specific power output of 100-200 W/kg of alloy for single stage and 150 - 300 W/kg of alloy for double stage MHHP system were achieved. The multihydride thermal-wave system has a low specific power output but it offers significant advantages like modest hardware effort, low pumping power and a wide operating temperature range.

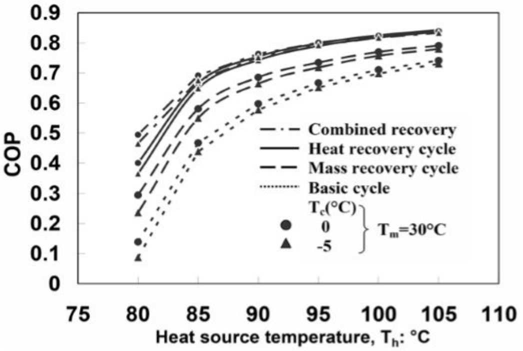


Fig. 4. Effect of Heat & Mass Recovery on Cooling System Performance.

VI. CONCLUSION

Metal hydrides are promising working materials for thermally driven solid sorption cooling machines with hydrogen as working fluid. The systems can cover a wide range of operating temperatures from cryogenic applications to comfort air-conditioning. A variety of heat sources from solar heat to automobile exhaust gases can be used to drive the cooling systems. In recent years various designs of such machines have been successfully demonstrated on a laboratory model or prototype scales. In fact, these can be most appropriate for small capacity portable or mobile cooling applications.

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