Magnetic Refrigeration- A Review- A boon for the coming generations

Dr. L.C.Singal[#1], Aishna Mahajan[#2], Rajwinder Singh[#3]
[#1]*Professor, Deptt.of Mechanical Engineering, Chandigarh Engineering College, Landran (Mohali), Punjab, INDIA*
[#2]*Associate Professor, Deptt. of Mechanical Engineering, Chandigarh Engineering College, Landran (Mohali), Punjab, INDIA*
[#3]*Assistant Professor, Deptt. of Mechanical Engineering, Chandigarh Engineering College, Landran (Mohali), Punjab, INDIA*

Abstract

Magnetic cooling is an old concept but being tried for day today applications in order to overcome the disadvantages of conventionally used vapor compression refrigeration systems regarding reduced power input and freedom from Ozone Depletion and Global Warming. Long back, it has been successfully applied in the cryogenic temperature ranges. Magnetic refrigeration is based on the magneto-caloric effect, a characteristic present in all magnetic materials and their alloys. Magnet caloric effect means that the temperature of a suitable material changes when magnetized or de-magnetized. Magnetization of a magneto-caloric material is equivalent to the compression of a gas (heating), while demagnetization is equivalent to expansion of a gas (cooling). The first most requirements are that these variations must be achievable speedily, repeatedly, reversibly with minimum energy losses.In this paper, the applicability of this method for room temperature refrigeration and air conditioning has been studied. Firstly, the magnetic refrigeration and vapor compression systems have been compared. Secondly, the magneto – caloric materials and their requirements has been listed.Thirdly, the effect of various parameters as strength of the magnetic field, regenerator configuration, temperature span and refrigerant fluid on the performance of magnetic refrigerationhas been discussed.Lastly and not the least, the advantages and disadvantages has been mentioned. Magnetic refrigeration seems to posses' great potential for future generations.

Keywords *–Magneto caloric material, Adiabatic magnetization, Adiabatic demagnetization, Regenerator, Fluid*

I. INTRODUCTION

As compared to conventional vapor compression refrigeration, magnetic refrigeration is simple, safe, quiet and compact. It has a higher cooling efficiency and is more eco-friendly because it does not use harmful ozone-depleting and global warming refrigerants (1,2,3). Cooling produced by using a magnet is called magnetic refrigeration. It is based on the magneto caloric effect.Magnet caloric effect means that the temperature of a suitable material changes when magnetized or de-magnetized. This effect has already been used to achieve extremely low temperatures (0.0001 K) and the temperatures ranges used in common cooling devices. The effect was first noticed by French physicist P.Weiss and Swiss physicist A. Piccar in 1917(4). The fundamental principle was suggested by P.Debye (1926) and W.Giauque in 1927(5).The first refrigerators working on magnetic refrigeration were constructed by many groups in 1933. When a magnet is applied to a material which can be magnetized under a magnetic field, the molecules of the material get arranged in a regular pattern and hence randomness of the molecules is decreased. It amounts to compression or ordered molecules occupy less space than disordered. Disorder changing into an ordered arrangement is exothermic. Now the hot salt is cooled with a fluid and then on demagnetization, the molecules acquire disordered arrangement which is endothermic. The salt is thermally insulated while being demagnetized; there will be a significant drop of temperature.The first most requirements are that these variations must be achievable speedily, repeatedly, reversibly with minimum energy losses.Themaximum cooling effectby demagnetization has been found ingadoliniumand its alloy ($Gd_5Si_2Ge_2$)andPraseodymium alloyed with nickel ($PrNi_5$)respectively(6). The new solid-state approach appears to be perfect form of cooling and refrigeration in the right direction.

II. MAGNETO-CALORIC EFFECT (MCE) MATERIALS

The magneto-caloric effect (MCE) will be maximum under a magnetic field when the solid is near its magnetic ordering temperature. Therefore the materials for magnetic refrigeration should have magnetic phase transition temperature near the application temperature as 22 to 27^{0}C in air conditioning and 0^{0}C in a refrigerator (7-12). This effect has been found to be maximum in ferro-magnetic materials (paramagnetic salts, gadolinium and its alloys) because these undergo a magnetic phase transition at Curie temperature which is around 20^0C. These materials are expensive. In February 2014, GE announced the development of a functional Ni-Mnbased magnetic refrigerator (13,14). Even this material is costly. Hence magnetic refrigeration is not likely to replace vapor-compression refrigeration till cheap and abundant magneto caloric materials are found. These materials should also have large magneto caloric effect over a larger range of temperatures under a magnetic field of two Tesla or less which can be produced with permanent magnets (15-27). Magnetic refrigeration have already produced lowtemperatures of 0.0001 k and 0.000001 K respectively using paramagnetic salts and by nuclear demagnetization. Since these low temperatures have limited laboratory applications only.Modern research is focused on near room temperature refrigeration by magnetic cooling.It will be possible only by the discovery of magneto caloric materials such asNiCoMnSb alloys with a higher concentration of Co decreases the phase change temperature (martensitic transition temperature) and also increases the MCE. More research is required to achieve a breakthrough in finding many more such suitable cheap materials. There are two types of magneto caloric materials namely FOMT (First Order Magnetic Transition) and SOMT (Second Order Magnetic Transition).

III. TABLE I

COMPARISON OF FOMT AND SOMT MAGNETO CALORIC MATERIALS [10-40]

Material → **Sr.No.↓**	**FOMT (First Order Magnetic Transition)**	**SOMT (Second Order Magnetic Transition)**
1.	A FOMT exhibits a discontinuity in the first derivative of the Gibbs free energy	A SOMT exhibits continuity in the first derivative, but exhibits discontinuities in a second derivative of the free energy.
2.	The magnetization effect in FOMT, which is the first derivative of the free energy with the applied magnetic field strength, is discontinuous	In a SOMT The magnetization effect in which is the first derivative of the free energy with the applied magnetic field strength, is continuous but the magnetic susceptibility, which is the second derivative of the free energy with the field, is discontinuous.
3.	The MCE, in a SOMT material, can be measured in terms of the adiabatic temperature change (ΔT_{ad}) or in terms of the isothermal magnetic entropy change (ΔS_M) upon magnetic field variations. MCE is measureable from the value of (ΔT_{ad}) or (ΔS_M).	The MCE, in a SOMT material, can be measured in terms of the adiabatic temperature change (ΔT_{ad}) or in terms of the isothermal magnetic entropy change (ΔS_M) upon magnetic field variations. However these changes (ΔT_{ad}) or (ΔS_M) are related to $(\partial M/\partial T)_H$ parameter. Therefore the MCE becomes maximum when $(\partial M/\partial T)_H$ reaches its maximum value i.e.around the Curie temperature in a ferromagnetic or near absolute zero in a paramagnetic.
4.	The FOMT materials show a simultaneous ordering of magnetic dipoles and a latent heat associated with the transition is released.	The SOMT materials show a relatively slow ordering of magnetic dipoles and a latent heat associated with the transition is released and gives relatively less MCE.
5.	There are large adiabatic temperature variations in most of the FOMT materials than that of SOMT.	There are less adiabatic temperature variations in most of the SOMT than that of FOMT.
6.	The temperature change in the SOMT materials is very slow and small because these experience a	The temperature change in the SOMT materials is almost instantaneous. There are no

	change in structure which takes much longer time.	structure changes during magnetization or demagnetization.
7.	Hysteresis losses are high.	Hysteresis losses are almost negligible.
8.	Most of the FOMT are brittle and undergoes large volume changes on magnetization or demagnetization and hence develop cracks. These broken pieces may clog the regenerator bed, reduces the flow of the heat transfer fluid and decreases the cooling effect.	Most of the SOMT are not brittle and undergoes almost no volume change on magnetization or demagnetization. There is a continuous flow of the heat transfer fluid and results in increased cooling effect.
9.	Example for FOMT is MnAs compounds. The Curie temperature (T_c) of these alloys varies in the range of 220-318 K. The compound $MnFeP_{0.45}As_{0.55}$ undergoes (T_c = 296 K) a first order transition from the paramagnetic to the ferromagnetic phase.	Example of SOMT is gadolinium (from lanthanide group of elements). At the, Gd undergoes a second order paramagnetic – ferromagnetic phase transition at a Curie temperature (T_C) of 294K. Alloys composed of gadolinium, silicon and germanium exhibit a much larger magneto caloric effect than that of Gd alone at the room temperature.
10.	The Curie temperature can be adjusted by varying the fraction of silicon	The Curie temperature can be adjusted by varying the fraction of silicon
11.	The thermal conductivity of FOMT is significantly lower than that of SOMT.	The thermal conductivity of SOMT is significantly higher than that for FOMT.
12.	FOMT are costly.	SOMT are costly.

In general, SOMT materials seem to be better. But lot of research is required to discover cheap magneto caloric materials having large temperature ranges on magnetization as well as on demagnetization coupled with durability, convenience and safe disposal after use.

IV. REGENATOR

The Magneto Caloric Material is magnetized and heated up under a magnetic field and losses heat to the surroundings with the use of a fluid (water). It demagnetizes as well as cooled when the magnetic field is removed, the fluid circulated is cooled. It is then circulated round the space to be cooled like chilled water used in central air conditioning applications. Regenerators of various configurations have been tried. In the regenerator, fluid is alternately heated and cooled. Thus regenerator is working as condenser on magnetization and as evaporator on demagnetization.More research is also required in the design of regenerators to make magnetic refrigeration a reality.

V. ROOM TEMPERATURE MAGNETIC REFRIGERATION [28-50]

Ames Laboratory researchers Karl A. Gschneidner Jr. and others are developed the first material that can work in a magnetic refrigerator at room temperature without the need of superconducting magnets or liquid helium. They also developed a magnet with twice the magnetic strength of previous designs. This may help to achieve widespread commercial applications at the Room-Temperature with magnetic refrigeration. The material developed was gadolinium by adding silicon and germanium (Gd_5 Si_2 Ge_2 alloy) and then they developed the magnetic refrigerator. In this, the refrigerator consists of a wheel that contains sections filled with the gadolinium alloy. The wheel revolves around a high-powered, rare-earth permanent magnet. As it revolves, it passes through a gap in the magnet at the precise point where the magnetic field is concentrated. When exposed to this field, the gadolinium alloy in the wheel becomes a magnet and is heated up. After entering the field, water is circulated to draw the heat out of the metal. On further rotation as the gadolinium alloy leaves the magnetic field, the material cools further. A second stream of water is itself cooled by the gadolinium alloy. This water is then circulated through the space to be cooled. It has also been discovered that magneto caloric effect is maximum at Curie temperature whose range is which very near to atmospheric temperature. Therefore, day is not far off when magnetic refrigeration may become order of the day in common applications.

Whirlpool's developed and used of an iron-based alloy to provide the magnetic refrigeration in a domestic fridge. This iron based alloy reduces the technology cost considerably over the rare-earth magnets such as gadolinium which were used by the initial researchers causing extremely low temperatures by adiabatic demagnetization.

VI. COMPARISON BETWEEN MAGNETIC COOLING AND CONVENTIONAL VAPOR COMPRESSION REFRIGERATION

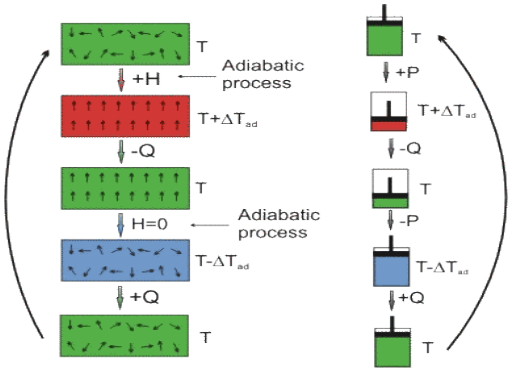

Fig 1: Magnetic Cooling Vs Conventional Vapor Compression Refrigeration [51]

In Fig.1, $H$is the strength of the externally applied magnetic field

$+P$is the increase of pressure (compressor)

$+\Delta T_{ad}$rise of temperature adiabatically (compression process)

$-Q$ is the heat lost to ambient (condenser)

-P decrease of pressure (expansion device)

$-\Delta T_{ad}$decrease of temperature (expansion process)

H=0 adiabatic process

$+Q$ is the cooling effect (evaporator)

The magnetic cooling cycle is similar to the vapor compression refrigeration cycle. The strength of magnetic field is alternately increased and decreasedinstead of increase and decrease in pressure of the refrigerant.There will be more clarity with the following graphical illustrations.

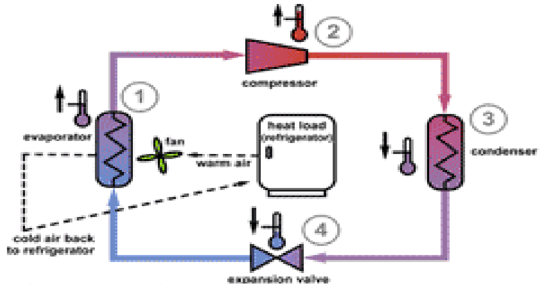

Fig 2. Vapour Compression Refrigeration Cycle [52]

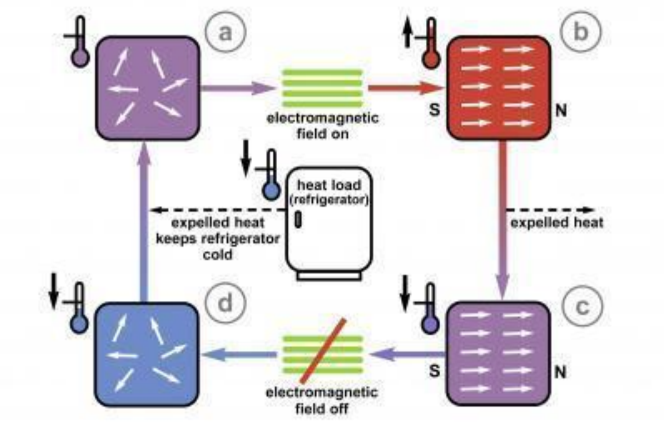

Fig 3. Magnetic Refrigeration Cycle [52]

The cycle shown above is the conventional vapor compression refrigeration cycle. It uses the phase changes of a refrigerant such as "Freon" to move the heat from lower temperature to the higher temperature. The cycle shown below is the magnetic refrigeration cycle which uses an adiabatic magnetization and adiabatic demagnetization to obtain cooling on magneto caloric material. It has been established that magnetic refrigeration consumes 20 % less energy than consumed in the vapor compression cycle for the same amount of cooling obtained. The cycle shown below is for adiabatic magnetization and adiabatic demagnetization of a special solid material, Gadolinium and its alloys or a Nickel Manganese Indium alloy.

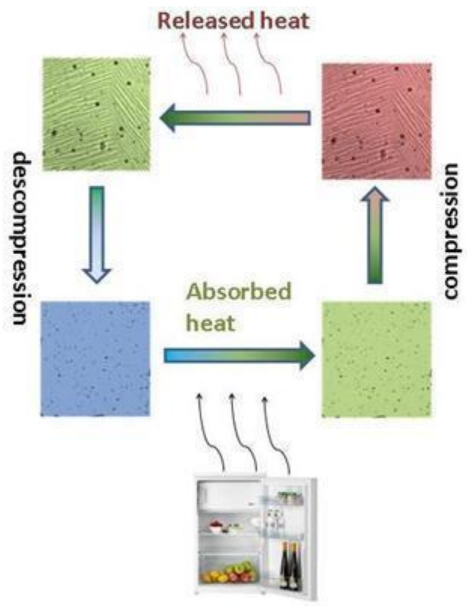

Fig 4. Adiabatic Magnetization And Adiabatic Demagnetization [53]

The operation of a standard adiabatic demagnetization refrigerator (ADR) or magnetic refrigeration will be achieved with the following four steps:

(i) Apply a strong magnetic field to the magnetization material (refrigerant) in the thermally insulated condition with no fluid flow, forcing its various magnetic dipoles to align, gives out heat energy and raise its temperature. At the beginning of the cycle, the fluid is at the cold temperature T_c.

(ii) Maintaining the applied field, the fluid is circulated through the regenerator. The fluid absorbs heat from the material and transports it towards the hot heat exchanger till its temperature is above the heat rejection temperature T_h.

(iii) Keeping the refrigerant thermally insulated in the magnetized condition, the magnetic field is switched off in the absence of the fluid flow. Disordering being endothermic decreases its temperature much below the temperature of the heat sink.

(iv) Now circulate the fluid for getting cooled and the cooled fluid is circulated in the space to be cooled as is conventional in central air conditioning system. Thus refrigeration will be obtained. These four steps will be repeated time and again for continuous cooling.

VII. ADVANTAGES OF MAGNETIC REFRIGERATION

(i) It is more efficient and reduces the power consumption by 20 to 30 %.

(ii) Solid state refrigerants are eco-friendly as these do not cause Global Warming and Ozone Depletion.

(iii) There will be no leakage or contamination of the refrigerant.

(iv) This system is simple, safe and durable.

(v) System running cost is less.

(vi) It has fewer maintenance problems because there is no moving part.

(vii) Disposal of such systems will be simple and cost effective.

(viii) Performance has been found to be best near Curie temperature which is nearly 20^0C

VIII. DISADVANTAGES OF MAGNETIC REFRIGERATION

(i) Large heat transfer surfaces (heat exchangers) are required because of low temperature span on magnetization as well as in demagnetization.

(ii) Strong magnets are required which are costly.

(iii) Magneto caloric materials till date are expensive.

(iv) System will be overall bulky(volume 2 to 3 times), heavy (weight 3 to 4 times) and costly (2 to 3 times).

(v) In some solid materials having large temperature span, performance has been to decrease.

IX. CHALLENGES IN MAGNETIC REFRIGERATION

Few products have come to the market but still there are lots of challenges that need to be addressed before there is large-scale application of magnetic refrigeration. One of the main issues is the supply of magneto caloric materials, which are available in limited quantity. Identify new materials or reduce the content of MCE would increase viability of this technology. The fabrication process is not yet optimized and production costs are still high, Development of prototypes for various specific applications needs to take place.

Although there is a lot of research work done, the current market development is not fully mature. Cool-tech Applications and Nextpac are trying to enter this field working on heat-pump applications. In 2015, Cool-tech Applications produced a 150-700W product as part of a refrigeration system and the first tests will be carried out at end users' sites, such as supermarkets, in 2015 only.Lot of research is being carried out on magnetic refrigeration in Camfridge.Other multinationals working on similar technologies include Whirlpool, Electrolux, Astronautics, GE Appliances, Samsung, Erasteel, Sanden, Chubu, BASF and VAC.

Magnetic refrigeration technology is very promising. But still it is not yet ready for market. It is expected that there will be a major breakthrough in this field in the near future. It does have potential to reduce energy use and operate without the use of refrigerants causing Global Warming and Ozone Depletion. All these make it an exciting proposition.

X. CONCLUSIONS

Based on the research carried out, the following conclusionscan be drawn.

(i) Magnetic cooling devices can offer a similar or improved performance than traditional vapor compression refrigeration systems.

(ii) Presently magnetic cooling devices are much heavier (3 to 4 times) and voluminous(2 to 3 times) than traditional systems.

(iii) Magneto caloric materials already tried havelow adiabatic temperature changes which can be produced with permanent magnets. It has resulted in 7- 9 times fluid flow than in an equivalent compressor system.

(iv) There is more pressure drop resulting in high pumping cost.

(v) On increasing the adiabatic temperature span, performance decreases. It is a new challenge for its implementation.
(vi) The performance of magnetic cooling systems is highly dependent on the magnetic field swing (strength). For 1.5 T to 2.5 T magnetic swings, the requirements of material are halved. This magnetic strength requires the use of superconducting magnets.
(vii) Superconducting magnets are only feasible for large scale applications otherwise it will be a big drawback for magnetic refrigeration for common applications
(viii) Performance has been found to be best at Curie temperature which is around 20^0C. Thus it can be best suited for comfort air conditioning applications.
(ix) Presently there are number of contradictions in improving the performance of magnetic refrigeration. But the day these are overcome, it will be a boon for the coming generations because of the inherent advantages the magnetic refrigeration posses over the conventional vapor compression refrigeration systems.
(x) Use of hybrid technologies employing both magnetic cooling and vapor compression could complement each other, creating a more efficient and powerful device for those cases where the extra cost would be assumable, as in military applications and off-shore drilling platforms

XI. SUGGESTIONS FOR FUTURE RESEARCH

(i) Investigation for new magneto caloric materials with large MCE and durability are required as so far, no material has been found to outperform Gd and its alloys.
(ii) Investigations for the cheaper strong magnets are required.
(iii) Investigations are required for reduction in weight, volume and cost of the method.
(iv) Investigations into the more advanced regenerator geometries are to be carried out to get improved performance.

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