Centrum Rzeczoznawstwa Budowlanego

Open Access Journal
Modern Engineering 4 (2023) 38-49
journal homepage: https://mengineering.eu/

Modern Engineering

The Concept of a Novel Cold Storage Device Utilizing the Magnetocaloric Effect

Katarzyna KATANA[1], Andrzej GRZEBIELEC*[1]

[1] Warsaw University of Technology, Warsaw, Poland

Abstract

Cold storage poses many more problems than heat storage. This is due to the fact that the temperature range is smaller than in the case of heat storage facilities. The simplest example is that cold water chillers operate in the temperature range of 12/7 ºC and the heating system operates in the temperature range of 90/70 ºC. This means that at the start the volume in sensible heat is almost three times greater. For this reason, cold is rarely stored in the form of sensible heat. Phase change solutions (PCM) or physical reactions (adsorption) or chemical reactions (absorption) are much more frequently used. A completely different idea for improving the operation of cold stores is the use of magnetocaloric materials. These are materials that change temperature under the influence of a magnetic field. The article presents the concept of a cold store that cooperates with a heat exchanger made of magnetocaloric materials (pure Gadolinium). As a result of the preliminary analysis, it was determined that this combination of vapour compressor system and magnetocaloric heat exchanger allows for a reduction in energy consumption for storage purposes at the level of 58,6% in comparison to regular vapour compressor system.

Key words
cold storage, magnetocaloric material, gadolinium, Gd, energy efficiency, energy storage system

1. Introduction

Cold storage, just like heat storage, is a huge challenge for modern energy installations [1]. It is worth noting that the use of cold, e.g. for air conditioning, depends on daily and seasonal changes. This is caused by large daily temperature fluctuations in summer conditions. Therefore, it seems advisable that cold stores should be located next to each refrigeration or air conditioning installation - this would allow for smaller devices and also for reducing electricity consumption during peak hours. However, practice shows that this solution is not widely used. This phenomenon is associated with several problems. Working systems most often use water or water-glycol solutions to distribute cold [2]. This means that in order to store cold in the form of sensible heat, compressor systems must operate at lower temperatures - that is, also with a significantly lower efficiency coefficient *EER*. Which physically makes cold storage simply more expensive by 20-30%. The second problem in this type of solutions is the volume of storage tanks. Cold water chillers for air conditioning systems operate in Polish conditions at temperatures of 7/12 ºC (inlet/outlet respectively), which means that storing of 10 kWh cold requires a tank with a volume of 1.7 m^3.
Other solutions that can be used to store cold are devices that use phase change materials (PCM), or the phenomenon of adsorption [3]. Fig. 1 shows how the volume of the storage unit decreases depending on the technology used.

***Corresponding author:** E-mail address: (andrzej.grzebielec@pw.edu.pl) Andrzej GRZEBIELEC

Received 10 December 2023
Available online 31 December 2023
ISSN 2450-5501
Published by Centrum Rzeczoznawstwa Budowlanego

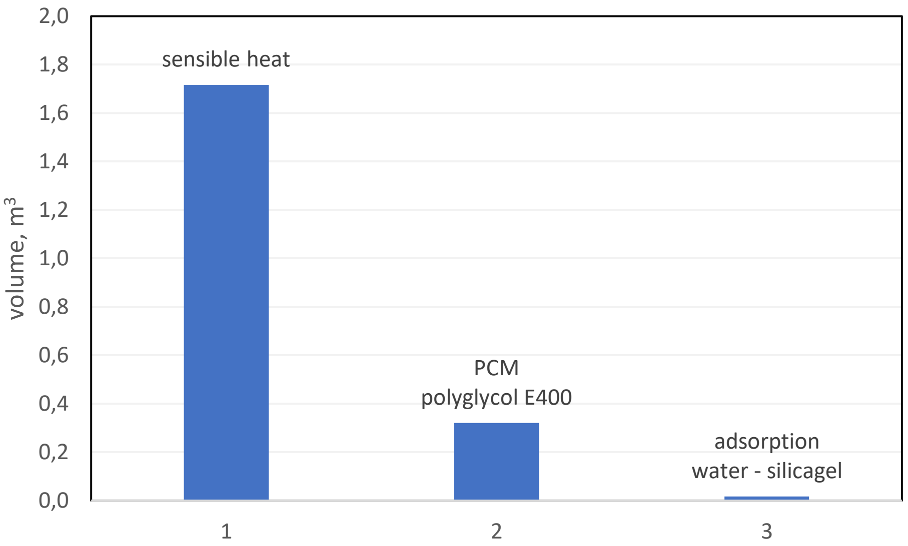

Figure 1. Comparison of cold storage methods for 10 kWh of cold

The solutions related to PCM or adsorption processes are also not free from problems. One of the main ones is the heat transfer problem. The devices require specially designed heat exchanger solutions. In the case of PCM, there are also noticed large pressure drops, and in the case of both PCM and adsorption, there is a problem with heat flow in the storage beds. This mainly concerns adsorption solution, because adsorption materials are porous one.

1.1.Magnetocaloric devices

Materials, due to their magnetic properties, are divided into ferromagnetics, paramagnetics, and diamagnetics. It is important to note that these properties are temperature - dependent. From the thermal engineering standpoint, the most significant is the Curie temperature - the temperature at which the body ceases to behave like a ferromagnet and starts behaving like a paramagnet. At this temperature, the greatest magnetocaloric effect is observed as well. Upon the application or removal of an external magnetic field, which can be created using an electromagnet, magnetic materials undergo isothermal magnetic entropy changes, as well as adiabatic temperature changes. This exact phenomenon is known as the magnetocaloric effect and cand be used as an energy – efficient and environmentally friendly refrigeration technology. The change in the body's temperature, due to the action of the magnetic field intensity, can be practically utilized in several energy processes. The use of heat exchangers made of such materials enables heat exchange efficiency to surpass 100 %. It is also an environmentally friendly method [4]. Particularly prospective application is their use in heat or cold storage processes. In current heat storage systems, the charging temperature is always higher than the discharging temperature. By employing magnetocaloric materials, it is possible to combine the charging process with the activation/deactivation of the magnetic field and then link these processes with activation/deactivation during discharging, achieving a discharging temperature close to the charging temperature. The magnetocaloric effect can be successfully utilized to improve the efficiency of many processes commonly used in energy and refrigeration, especially in cyclically operating devices utilizing regenerators - in which the regenerators can be constructed from magnetocaloric materials [5]. Approximately 15% of worldwide energy consumption involves the use of refrigeration. Compared with conventional gas compression/expansion cooling technology, magnetic refrigeration is environmentally friendly and efficient. Magnetic refrigeration has already been shown to achieve 60% of Carnot efficiency, while the gas compression systems can reach only 20%–40% [6].

1.2.Magnetocaloric effect

Magnetocaloric effect, MCE [7] manifests itself in the fact that when a magnetic material is subjected to a sufficiently strong magnetic field, the magnetic moments of the material's atoms are reoriented. This causes the temperature of the material to change. However, when the external magnetic field is removed, the material temperature returns to its original value. This phenomenon is related to the change in magnetic entropy ΔS_m and adiabatic temperature change ΔT_{ad} [8], which can be written in the form of Maxwell's equation.

$$\left(\frac{\partial S}{\partial H}\right)_T = -\left(\frac{\partial M}{\partial T}\right)_H \tag{1}$$

where:

S – entropy;

H – magnetic field range;

M – magnetization;

T – temperature.

The entropy and the temperature changes can therefore be determined according to the equations:

$$\Delta S_m(T, \Delta H) = \int_{H_0}^{H_1} \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \tag{2}$$

$$\Delta T_{ad}(T, \Delta H) = -\int_{H_0}^{H_1} \frac{T}{C_{P,H}} \left(\frac{\partial M(T,H)}{\partial T}\right)_H dH \tag{3}$$

The magnetocaloric effect can be both positive and negative. Positive means that as the magnetic field intensity increases, the change in magnetism is negative, but the temperature difference is positive. This phenomenon is called the simple magnetocaloric effect. For some antiferromagnets and ferrimagnets, with increasing magnetic field strength, the change in magnetism is positive, which causes the change in temperature to be negative [8]. This is called the reverse magnetocaloric effect. For the application, it does not matter which of the two effects takes place, as it only causes a shift in the phase of the magnetic field periods.

Temperature affects the magnetic properties of materials. Increasing the temperature of a solid causes an increase in the magnitude of the atom's thermal vibrations. In the case of ferromagnetic materials, both antiferromagnetic and ferromagnetic, atomic thermal motions oppose the coupling forces between adjacent atomic dipoles, causing some shifting, regardless of whether an external field is applied. This reduces the magnetization of ferromagnetic and antiferromagnetic materials. The magnetization is highest at 0 K, the temperature at which thermal vibrations are minimal. As the temperature increases, the magnetization gradually decreases and then suddenly drops to zero at the so-called Curie temperature (T_C). Hence, T_C can be defined as the lowest temperature at which the magnetization of the material (magnetism) in the absence of an external field is zero. Above the T_C temperature the thermal vibrations, i.e., the temperature, are strong enough to randomly align the spins, while below the T_C spontaneous magnetization occurs. At temperatures above T_C, ferromagnetic materials become paramagnetic [5], [9], [10].

Figure 2 shows a typical change in magnetization, change in entropy difference, and change in adiabatic temperature difference as a function of body temperature.

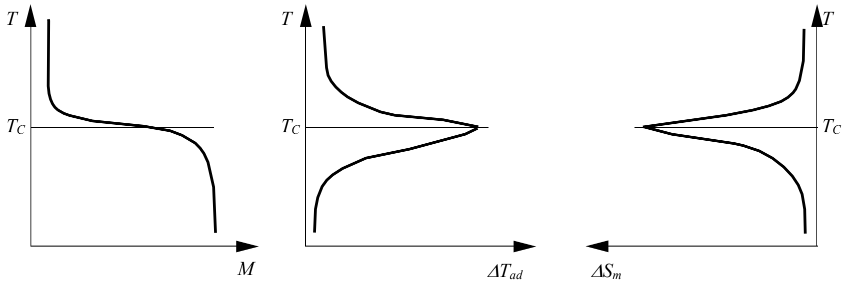

Figure 2. Changes in magnetization M, change in adiabatic temperature difference ΔT_{ad}, and change in entropy difference ΔS_m as a function of body temperature [5]

At the same time, it should be remembered that the value of the change in entropy and adiabatic temperature depends on the external magnetic field intensity.

Knowing the entropy change line and the adiabatic temperature, it is possible to determine the T-s characteristics for the magnetocaloric material, which enable the design of magnetic refrigeration devices or the construction of cold storage unit. Fig. 3 shows the theoretical lines of constant magnetic field intensity in the magnetocaloric material on the T-s diagram.

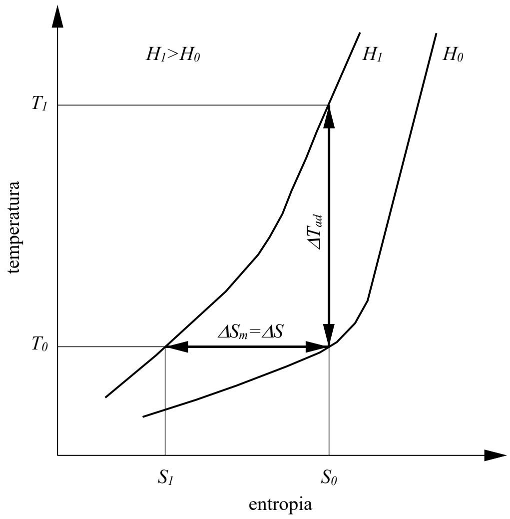

Figure 3. T-s diagram for a magnetocaloric material [5]

1.3. Magnetocaloric materials

Until recently a Gadolinium (Gd) rare-earth metal with large magnetocaloric effect has been considered as the most active magnetic refrigerant in room-temperature magnetic refrigerators, but its usage is somehow commercially limited because the cost of Gd is quite expensive. [11]. The search for a cheaper material that displays a greater magnetocaloric effect led to the discovery of $Gd_5Si_2Ge_2$ which's magnetocaloric effect is twice the gadoliniums. Nevertheless, despite these new discoveries, the vast majority of cooling prototypes still use Gd as the cooling material, mostly due to the excellent reproducibility of its magnetocaloric effect. [12] In the project, the Curie temperature should be within the range of 273 K – 293 K. This excludes the usage of other popular magnetocaloric materials as shown in Tab 1.1. Gadolinium has been chosen due to its potential for widespread application in room temperature refrigerators - Curie temperature of pure Gadolinium is 292 K. Another key aspect is change of the adiabatic temperature, the greater the change, the better potential for a magnetocaloric heat exchanger.

Table 1. Magnetocaloric materials [11], [12], [13], [14]

Magnetocaloric material	T_C [K]
Fe (Iron)	1043
Ni (Nickel)	627
$La_{0.67}Ba_{0.33}Mn_{.1.05}O_3$	347
$Gd_5Si_2Ge_2$	340
MnAs (Manganese Arsenide)	318
Gd (Gadolinium)	292
LaFeSi	290
$LaFe_{11.8}Si_{1.2}$	250
Tb (Terbium)	221
Dy (Dysprosium)	88
$GdCl_3$	2,2

2. Energy storage unit conception

The proposed system has been presented in figure 4. It consists of a storage tank where the cold is stored at a temperature lower than supplied by the chiller, a heat exchanger operating periodically, constructed with Gadolinium, and a chilled water chiller that cools the water to a temperature of 7°C

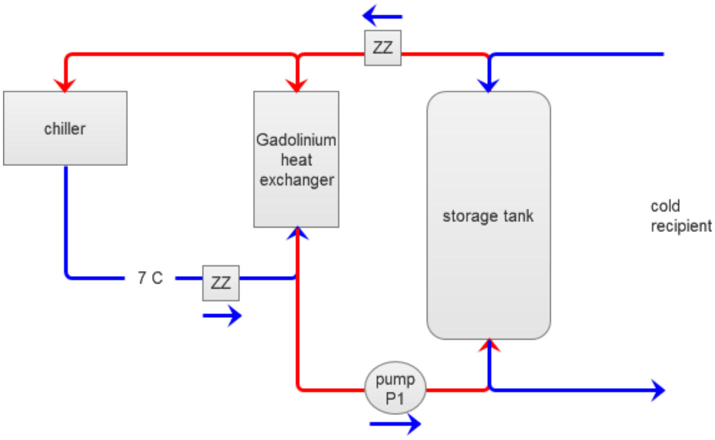

Figure 4. The analyzed cold storage system

The Gadolinium heat exchanger has been designed in such a way that it consists of a cube-shaped body with drilled holes through which cold water will flow. The entire exchanger is located between the poles of the electromagnet in figure 5.

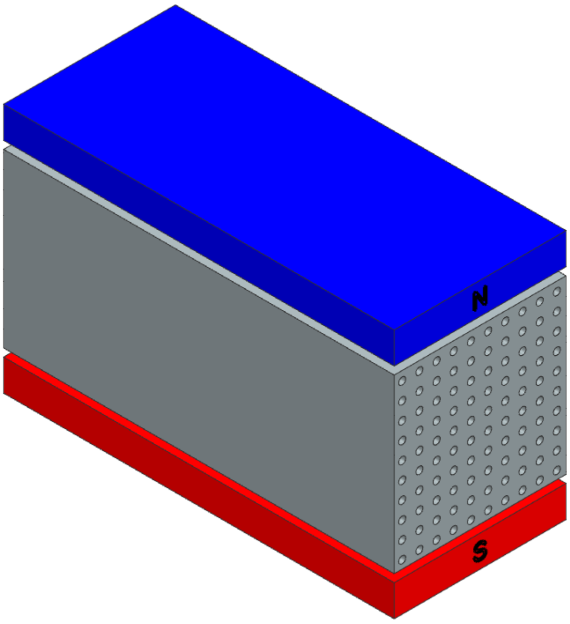

Figure 5. Designed heat exchanger

The magnetic refrigeration cycle is a continuous thermal transient process. One could visualize this transient process as a thermal wave that passes through the active material every half cycle. The heat of magnetization is removed, and the load is cooled periodically by a chiller. [15] The heat exchanger consists of the magnetocaloric material and working fluid, such as Gadolinium and water.

The work of cycle of the heat exchanger consists of several stages:

1. The exchanger is filled with warm water from the cooling reservoir (during this period, the chiller is turned off) – this process is short and is intended to displace the cold water at a temperature of 2°C from the heat exchanger.
2. The electromagnet is activated, causing the temperature of Gadolinium to rise. Pump P1 is turned off, and the chiller is turned on.
3. The chiller operates until the Gadolinium reaches a temperature of 7°C.
4. The electromagnet is turned off (resulting in a decrease in the temperature of Gadolinium), the chiller is turned off, and pump P1 remains off.
5. The process continues until the water temperature reaches 2°C and the entire process repeats from the beginning.

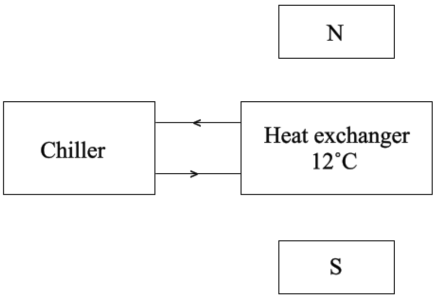

Figure 6. Initial state

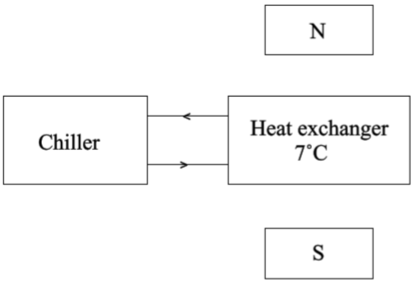

Figure 7. Cooling down heat exchanger meterial by chiller (under magnetic field)

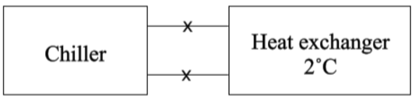

Figure 8. Removing the magnetization (heat exchanger temperature drops)

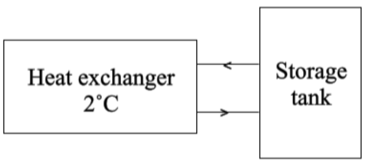

Figure 9. Transport of cold water to storage tank

2.1. Heat transfer in Gadolinium HX during water flow

The change in the temperature of gadolinium, from which the heat exchanger is made, when the water flows through it is expressed by the equation:

$$\frac{\partial T_{Gd}}{\partial t} m_{Gd} \cdot c_{p,Gd} = \dot{Q}_w \quad (4)$$

where:
m_{Gd} –Gadolinium mass;
$c_{p,Gd}$ –specific heat of Gadolinium;
T_{Gd} – Gadolinium temperature;
t – time;
$\dot{Q}_w$ - heat transferred from gadolinium to water, calculated from equation;

$$\dot{Q}_w = h \cdot A \cdot (T_{Gd} - T_w) \quad (5)$$

where:
h - heat transfer coefficient;
A – heat transfer area;
T_{Gd} – Gadolinium temperature;
T_w – water temperature.

The heat exchanger was divided into pieces of finite length, and equation 4 was solved by the finite difference method:

$$\frac{\partial T_{Gd}}{\partial t} = \frac{T_{Gd}(t_0+\Delta t) - T_{Gd}\,(t_0)}{\Delta t} \quad (6)$$

Therefore, equation (4) changes into:

$$\frac{T_{Gd}(t_0+\Delta t) - T_{Gd}\,(t_0)}{\Delta t} m_{Gd} \cdot c_{p,Gd} = h \cdot A \cdot (T_{Gd}(t_0) - T_w) \quad (7)$$

this allows to calculate temperature of the body in each time step:

$$T_{Gd}(t_n + \Delta t) = T_{Gd}\,(t_n) + \frac{h \cdot A \cdot (T_{Gd}(t_n) - T_w(t_n))}{m_{Gd} \cdot c_{p,Gd}} \Delta t \quad (8)$$

The capacity received by the water is also the required cooling capacity of the chiller:

$$\dot{Q}_w = h \cdot A \cdot (T_{Gd} - T_w) = \dot{m}_w \cdot c_{p,w}\left(T_{w,out} - T_{w,in}\right) \quad (9)$$

where:
$\dot{m}_w$ – water mass flow;
$c_{p,w}$ – water specific heat;
$T_{w,in}$ – water temperature at the inlet;
$T_{w,out}$ – water temperature at the outlet.

2.2. Change in magnetic field intensity

The relative cooling power (RCP) is a parameter used to identify a suitable magnetocaloric material for magnetic refrigeration applications. In an ideal refrigeration cycle, RCP is the amount of heat transferred between hot and cold reservoirs [16]. The RCP, based on the magnetic entropy change, is calculated by the equation:

$$RCP = -\Delta S_{M,max}\ x\ \delta T_{FWHM} \tag{10}$$

where:
δT_{FWHM} - the full width at half-maximum of the ΔS–T curve.

According to experimental data for Gd [17], there was estimated RCP coefficient as a function of magnetic Induction *B* in form of:

$$RCP = 57.073 \cdot B + 5.8392 \tag{11}$$

where:
B – magnetic induction (T).

The amount of energy required to generate magnetic induction in a known medium is equal to

$$E = \frac{1}{2} \cdot B^2 \cdot V \cdot \mu \tag{12}$$

V – volume of the magnetized region (m^3)

μ – magnetic susceptibility (for Gd μ is $13{,}5\ \times\ 10^{-6} - \frac{m^3}{kg}$).

3. Results

The calculations were carried out for a gadolinium block with dimensions of 220 x 220 x 500 mm, in which 100 holes with a diameter of 9.3 mm were drilled. During the water flow, water with a flow rate of 0.15 $\frac{kg}{s}$ passed through the heat exchanger. The mass of gadolinium was 164.35 kg, and the mass of water was 3.40 kg. Under these conditions, the following temperature changes were obtained.

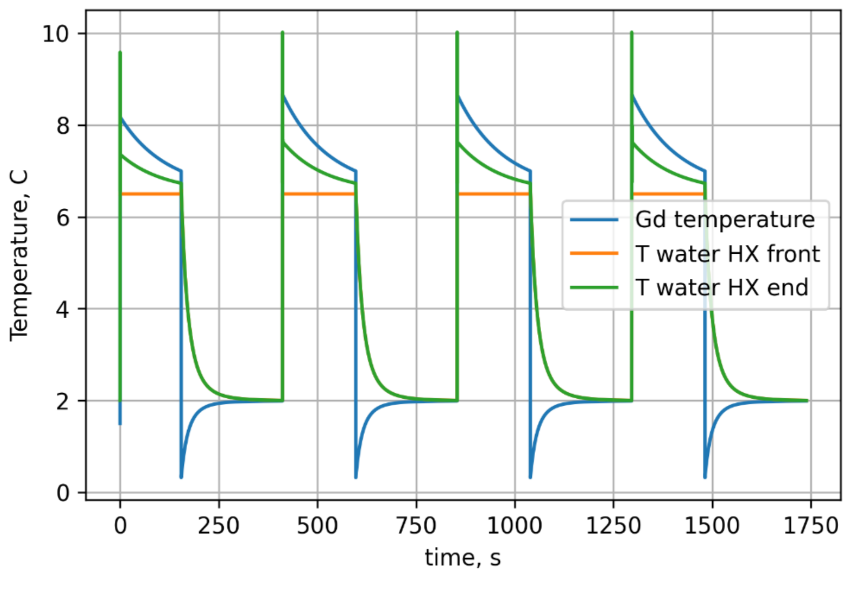

Figure 10. Temperature changes during cyclic operation

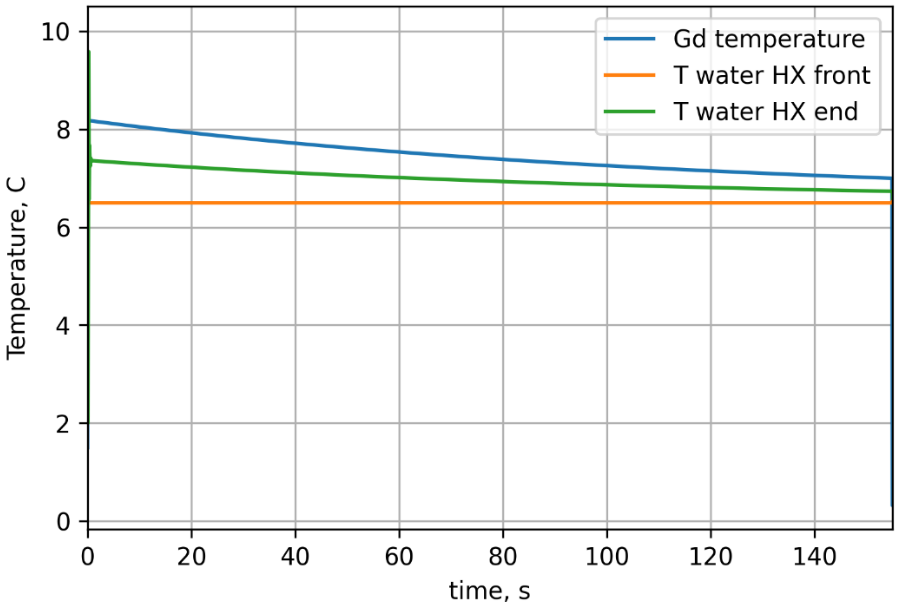

Figure 11. Temperature changes during the process of cooling Gadolinium by the chiller

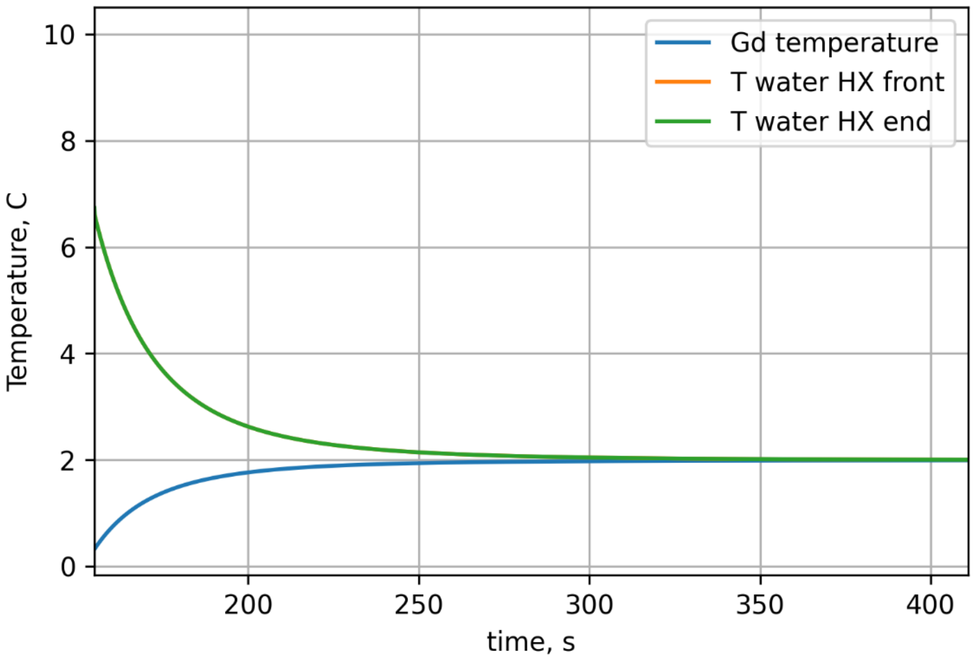

Figure 12. Temperature change during the process of equalizing temperature after a change in magnetic field intensity

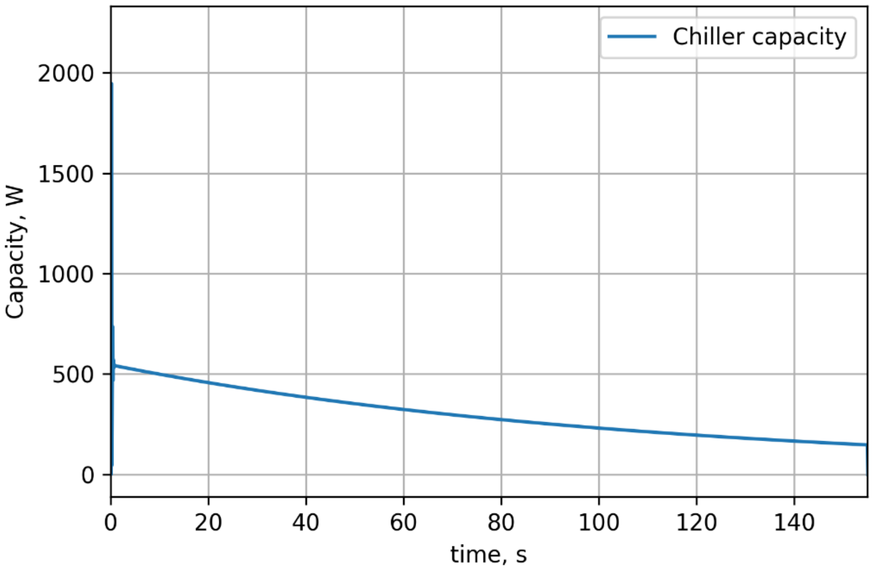

Figure 13. The cooling capacity during one cycle

The total cold energy supplied by the chiller in one cycle was calculated as:

$$q_{chiller} = 13738 \frac{J}{kg\ of\ water}$$

4. Conclusions

As part of the analysis, the results of the study on the cooling system utilizing the magnetocaloric effect were presented. This solution enables the cooling of fluids to a temperature lower than that achievable by the chiller. Moreover, the cooling mechanism itself is more energy-efficient than direct cooling by the chiller. Cooling chilled water from 7°C to 2°C requires electrical energy of 5,29 kJ per kilogram of water, while for the magnetic solution, it is only 2,19 kJ per kilogram of water. This is primarily the energy associated with the chiller, whose task is to cool the mass of gadolinium. According to the equation 12, the amount of magnetic energy needed to change the magnetic field of gadolinium is only $3{,}24 \times 10^{-4} \frac{\mathrm{J}}{kg}$.

This allows to conclude that a lower water temperature by 5 K was achieved at a energy cost 58,6% lower. The results also show that this solution can be used not only to store cold but also to increase the efficiency of compressor refrigeration systems during regular operation.

Acknowledgement

This work was carried out within the Excellence Initiative Research University of Warsaw University of Technology, Grant title: The use of magnetocaloric materials in energy processes.

References

[1] Y. Sha, W. Hua, H. Cao and X. Zhang, "Properties and encapsulation forms of phase change material and various types of cold storage box for cold chain logistics: A review," *Journal of Energy Storage,* vol. 55, p. 105426, 2022.

[2] A. Tafone and A. Romagnoli, "A novel liquid air energy storage system integrated with a cascaded latent heat cold thermal energy storage," *Energy,* vol. 281, p. 128203, 2023.

[3] M. Jaworski, M. Bednarczyk and M. Czachor, "Experimental investigation of thermoelectric generator (TEG) with PCM module," *Applied Thermal Engineering,* vol. 96, pp. 527-533, 2016.

[4] V. Franco, J. Blázquez, J. Ipus, J. Law, L. Moreno-Ramírez and A. Conde, "Magnetocaloric effect: from materials research to refrigeration devices.," *Prog. Mater. Sci.,* pp. 112-232, 2108.

[5] J. R. Gomez, R. F. Garcia, A. D. M. Catoira and M. R. Gomez, "Magnetocaloric effect: A review of the thermodynamic cycles in magnetic refrigeration," *Renewable and Sustainable Energy Reviews,* vol. 17, pp. 74-82, 2013.

[6] F. Kong and A. Inoue, "Iron-Based Magnetocaloric Materials," *Encyclopedia of Smart Materials,* pp. 433-439, 2022.

[7] M.-H. Phang and S.-C. Yu, "Review of the magnetocaloric effect in manganite materials," *Journal of Magnetism and Magnetic Materials,* vol. 308, no. 2, pp. 325-340, 2007.

[8] M. Duraj and A. Szytuła, "Własności magnetyczne i efekt magnetokaloryczny w związkach R1-xR'xMn2Ge2," *Czasopismo Techniczne. Nauki Podstawowe,* vol. 107, no. 1, pp. 57-70, 2010.

[9] K. A. Gschneidner Jr, V. K. Pecharsky and A. O. Tsokol, "Recent developments in magnetocaloric materials," *Reports on Progress in Physics,* vol. 68, p. 1479, 2005.

[10] E. Brück, "Developments in magnetocaloric refrigeration," *Journal of Physics D: Applied Physics,* vol. 38, p. R381, 2005.

[11] M. Phan, "Review of the magnetocaloric effect in manganite materials," *Journal of Magnetism and Magnetic Materials,* pp. 325 - 340, 2007.

[12] Q. Badosa, L. Mañosa, E. Vives and A. Planes, "Demagnetizing field-induced magnetocaloric effect in Gd," *J. Appl. Phys.,* p. 134, 2023.

[13] H. Zhang, R. Gimaev, B. Kovalev, K. Kamilov, V. Zverev and A. Tishin, "Review on the materials and devices for magnetic refrigeration in the temperature range of nitrogen and hydrogen liquefaction," *Physica B: Condensed Matter,* vol. 558, no. 1, pp. 65-73, 2019.

[14] C. Jäschke, M. Beyer, L. Schinke, J. Seifert and P. Schegner, "Power output of magnetocaloric materials during heat and cold decoupling by unidirectional fluid flow," *International Journal of Refrigeration,* vol. 155, pp. 67-72, 2023.

[15] E. Schroeder, G. Green and J. Chafe, Performance predictions of a magnetocaloric refrigerator using a finite element model, Los Angeles, 1989, pp. 1149 - 1155.

[16] A. El-Moez, A. Mohamed and B. Hernando, "Self-assembled impurity and its effect on magnetic and magnetocaloric properties of manganites.," *Ceram. Int,* p. 17044–17049, 2018.

[17] R. Essajai, N. Ennassiri, M. Balli, M. Zidane, E. Salmani, O. Mounkachi, M. Rouchdi, A. Abbassi, H. Ez-Zahraouy, .. A. Mzerd and N. Hassanain, "Revisiting the magnetic and magnetocaloric properties of bulk gadolinium: A combined DFT and Monte Carlo simulations," *Physica Scripta,* p. 96, January 2021.

[18] "BIAMAT CENTRUM," [Online]. Available: http://www.biamat.imn.gliwice.pl/produkty/materialy-magnetokaloryczne.html.

[19] J. Romero Gómez, R. Ferreiro Garcia, A. De Miguel Catoira and A. Romero Gómez, "Magnetocaloric effect: A review of the thermodynamics cycles in magnetic refrigiration.," *Renewable and Sustainable Energy Reviews,* pp. 74 - 82, 2013.

[20] T. Gottschall, M. D. Kuz'min, K. P. Skokov, Y. Skourski, M. Fries, O. Gutfleisch, M. Ghorbani Zavareh, D. Schlagel, Y. Mudryk, V. Pecharsky and J. Wosnitza, "Magnetocaloric effect of gadolinium in high magnetic fields," *Physical Review B,* p. 99, 19 April 2019.

[21] P. Pęczkowski, M. Łuszczek, E. Szostak, N. Kumar Chogondahalli Muniraju, A. Krztoń-Maziopa and Ł. Gondek, "Superconductivity and appearance of negative magnetocaloric effect in Ba1–xKxBiO3 perovskites, doped by Y, La and Pr,," *Acta Materialia,* vol. 22, no. 117437, 2022.