Energy Applications of Magnetocaloric Materials

Andrey Kitanovski

The need for energy-efficient and environmentally friendly refrigeration, heat pumping, air conditioning, and thermal energy harvesting systems is currently more urgent than ever. Magnetocaloric energy conversion is among the best available alternatives for achieving these technological goals and has been the subject of substantial basic and applied research over the last two decades. The subject is strongly interdisciplinary, requiring proper understanding and efficient integration of knowledge in different specialized fields. This review article presents a historical and up-to-date account of the energy-related applications of magnetocaloric materials and information about their processing and magnetic fields, thermodynamics, heat transfer, and other relevant characteristics. The article also discusses the conceptual design of magnetocaloric refrigeration and power generation systems and some guidelines for future research in the field.

1. Introduction

With the ongoing global trend of improving standard of living, economic growth, and population increase, the demand for cooling and air conditioning is expected to substantially increase over the next 30 years. Today, refrigeration and air conditioning account for about 17% of global electricity consumption,\(^1\) amounting to approximately 2000 TWh.\(^2\) If the energy efficiencies of the systems used for this purpose are not improved or new technologies are not introduced, the electricity consumption could triple by 2050.\(^2\)

The vast majority of residential, transportation, and commercial refrigeration; heat pumping; and air conditioning systems utilize vapor-compression technology,\(^3,4\) which can be regarded as a mature technology with optimized production and maintenance costs as well as safe and reliable operation. The energy efficiencies of refrigeration, heat pumping, and air conditioning systems are relatively high (for large-scale appliances, the second-law efficiencies can reach 60%).\(^5,6\)

However, small-scale appliances tend to have low efficiencies, with an average of 20% based on the Carnot cycle,\(^7\) revealing considerable room for improvement.\(^8\) The major problem of the vapor-compression technology is the adverse environmental impact of the currently utilized refrigerants, which contribute 7.8% of the total global greenhouse gas emission.\(^9,10\) Hence, substantial effort is being invested in the search for alternative refrigerants\(^11,12\) for providing everyday air conditioning and refrigeration. Although there are very limited environmentally friendly refrigerants,\(^13\) the current use of hydrofluorocarbons is expected to be globally phased out within the next 30–40 years.\(^14,15\) There has also been a search for alternatives to vapor-compression technology (Figure 1), with the current unprecedented degree of urgency pushing researchers to develop some radical technologies.\(^1,3,8,16,17\) One example is absorption and adsorption refrigeration, which holds a lot of promise when waste or renewable heat is available. Other thermally driven alternatives are ejector refrigeration systems, which, like sorption technologies, perform work without moving parts based on low-temperature thermal resources.\(^22,23\) An alternative technology presently available in the market is thermoelectric cooling, which utilizes the Peltier effect. This technology also performs work without moving parts, but suffers from a very low energy efficiency.\(^24\) It is, therefore, only suitable for specific markets and applications,\(^25–27\) especially for the cooling of electronics.\(^28\) Also worth mentioning here is thermoelectric refrigeration, which again operates without moving parts.\(^29,30\) However, the technology has the drawback of a low power density and the provided refrigeration is with only moderate efficiency.

Although new environmentally friendly refrigerants are expected to be found in the future, the energy efficiency of refrigeration and air conditioning also requires improvement. To a certain extent, this can be achieved through vapor compression. However, the limited potential of vapor compression leads us back to the search for alternative electrically or mechanically driven systems. Several researchers have concluded that caloric (ferroic)\(^31–34\) refrigeration and heat-pumping technologies, which are still in the research and development phase, are the most important option for the future.\(^8,3,16\) These solid-state technologies variously utilize magnetocaloric,\(^35–37\) electrocaloric,\(^38–40\) and mechanocaloric\(^41–43\) effects. A material that exhibits more than one of these effects is described as a multicaloric (multiferroic) material with multicaloric effects.\(^44–46\) The reversibility of the caloric effect, compared with the irreversible compression or expansion of a refrigera-
underscores the promises of caloric technologies. Moreover, as solid refrigerants, caloric materials do not represent an environmental threat as do all refrigerants used for vapor compression. Among the caloric (ferroic) technologies used for refrigeration, heat pumping, and air conditioning, magnetocaloric energy conversion is by far the most developed.

As implied, the efficient utilization of energy for cooling and air conditioning using environmentally friendly refrigerants is not the only important issue; how the process impacts the environment is also important. The introduction of different renewable energy technologies and the elimination of the use of fossil fuels are critical in this regard. One of the important factors considered in energy production is the regeneration of the huge amount of thermal energy contained in waste heat\cite{47,48} and the utilization of renewable heat.\cite{49,50} The best established large-scale technology for the conversion of waste or renewable heat to power (besides steam turbines) is based on the Organic Rankine Cycle (ORC).\cite{51-53} However, because devices that operate on this cycle use refrigerants, they also have adverse environmental implications.\cite{54-56} Other relevant technologies that have been developed include the Kalina\cite{57} or air-bottoming cycle and carbon dioxide-based power cycles.\cite{58,59} For small-scale kilowatt-range power requirements, Stirling engines\cite{60-62} and small ORC\cite{63} systems are currently under development and approaching the application phase. However, the vast majority of waste thermal energy sources are widely dispersed and at relatively low temperatures (below 100 °C) or are most suitable for micro-scale exploitation in the milliwatt to 1 kW range. In addition, they are often available in special environments such as the exhaust of a car or furnace, electronic devices and systems, photovoltaic-thermal or concentrated photovoltaic devices, and others. Existing technology for exploiting such heat sources is not cost or energy efficient, nor can they be adapted or physically implemented on a small scale. This is one reason why researchers are particularly focusing on solid-state technologies;\cite{64} the most advanced and most commonly applied examples of these are thermoelectrics, which exploit the Seebeck effect.\cite{65-67} Recent advances along this line include the development of new materials and fabrication methods,\cite{68,69} the development of flexible modules,\cite{70-72} and thermoelectric nanogenerators.\cite{73} Thermoelectric technology systems do not have moving parts, operate over different temperature ranges, and the flexibility of the utilized modules enables a broad variety of applications. However, despite the important

Figure 1. Non-vapor-compression refrigeration and air conditioning technologies.
improvements\textsuperscript{[66,74]} that have been achieved over the last 20 years, thermoelectric systems still have the disadvantage of low energy conversion efficiency. This, together with the rapid development of knowledge in the fields of materials science and physics, has diverted the attention of researchers to other solid-state technologies. In addition to the conversion of mechanical energy to electrical energy through piezoelectric,\textsuperscript{[75,76]} magnetoelectric,\textsuperscript{[77]} magnetostrictive,\textsuperscript{[78]} triboelectric,\textsuperscript{[79,80]} and electrostrictive\textsuperscript{[81]} effects, various technologies have been developed for the solid-state harvesting of thermal energy,\textsuperscript{[64,77,82,83]} including from low-grade thermal sources.\textsuperscript{[82,84]}

Over the last 20 years, in addition to thermoelectricity, much research on solid-state thermal energy harvesting (Figure 2) has also focused on thermionics\textsuperscript{[85–87]} and thermophotovoltaics.\textsuperscript{[89–90]} Researchers have also investigated new frontiers in spin-caloritronics\textsuperscript{[91,92]} spin-Seebeck\textsuperscript{[93,94]} and anomalous Nernst effects.\textsuperscript{[95,96]} However, with the rapid development of caloric (ferroic) materials and technologies for refrigeration and air conditioning, caloric (ferroic) power generation\textsuperscript{[64,77]} is being revisited and prototype devices are being developed.

Caloric power generation draws on specialized fields such as magnetocalorics (an aspect of thermomagnetics or pyromagnetics),\textsuperscript{[83,97,98]} electrocalorics (an aspect of pyroelectrics),\textsuperscript{[99–101]} and mechanocalorics (an aspect of thermoelastics).\textsuperscript{[102]} Similar to refrigeration, multicaloric (multiferroic) power generation has also attracted research interest.\textsuperscript{[103–105]} Because caloric (ferroic) materials allow the reversible caloric (ferroic) effect, it is obvious that their potential applications would go beyond refrigeration and air conditioning, reaching into power generation. Most of the related researches have focused on thermomagnetic energy conversion using magnetocaloric materials, which is also the interest of this review article.

1.1. Objectives of This Review Article

The current quest for energy efficient and environmentally friendly refrigeration, heat pumping, air conditioning, and thermal energy harvesting is more urgent than ever. Among the best available technologies for this purpose, magnetocaloric energy conversion, which utilizes magnetocaloric materials, represents a rapidly developing research field and a number of prototype devices have been developed.\textsuperscript{[35]} To bring this technology to the market, significant work is still required in the field of materials science, specifically for the processing of magnetocaloric materials, as well as the development of efficient and rapid heat transfer methods. Further research on rare-earth-free and recyclable magnetic field sources is also necessary, and the combination of such with engineering thermodynamics and related magnetocaloric principles would form the basis of an interdisciplinary development of energy-related magnetocaloric material technology. There have been numerous publications on magnetocaloric energy conversion technology, including review articles. However, a comprehensive understanding of the technology and presentation of up-to-date information from a critical perspective is required. Because of the strong interdisciplinarity of the subject, there is a need to outline the interaction between the different related scientific fields and put forward some guidelines for further research and development.

Addressing the foregoing need is the purpose of this review article. The work is expected to provide a fundamental understanding of magnetocaloric energy conversion, including a review of the state of the art of magnetocaloric materials and their processing, magnetic field sources, thermodynamics, and heat transfer, as well as the conceptual design of a magnetocaloric refrigeration or power generation device. This work will emphasize refrigeration and heat pumping near room temperature and magnetocaloric power generation, areas in which there exist important alternatives for thermal energy conversion technologies. A special section will also be dedicated to energy conversion using magnetocaloric materials under low temperature conditions, involving the liquefaction of gases such as hydrogen, propane, and natural gas.

1.2. How It Works

Magnetocaloric materials exhibit the magnetocaloric effect\textsuperscript{[106]} under a change in an externally applied magnetic field. This results in a change in the magnetic order of the material and a

Figure 2. Alternative solid-state technologies for thermal energy harvesting.
consequent decrease in the total entropy of the magnetic part. Under isentropic conditions, the total entropy of the material remains constant. Hence, the magnetic entropy change is compensated by a change in the lattice entropy, characterized by a change in the temperature of the magnetocaloric material. Because isentropic conditions are accompanied by adiabatic conditions, but not vice versa, the isentropic change in the temperature of the magnetocaloric material is also referred to as adiabatic temperature change, $\Delta T_{ad}^{\text{ad}}$. [107,108] If the magnetization of the magnetocaloric material is performed under isothermal conditions, the lattice entropy will remain constant. Consequently, the magnetic entropy change will result in an isothermal total entropy change $\Delta s_m = \Delta s$. [107,108] To utilize the magnetocaloric effect for refrigeration or heat pumping, it is necessary to execute the thermodynamic cycle close to the Curie temperature of the magnetocaloric material, at which the magnetocaloric effect is maximized. As a simple presentation of the refrigeration cycle, an analogy between magnetocaloric refrigeration and gas refrigeration is shown in Figure 3. The inverse of refrigeration is magnetocaloric power generation, also known as thermomagnetic power generation. The refrigeration cycle can also be simplified by the analogy of the ideal gas power cycle. It should be noted that, although gas refrigeration and power cycles are usually driven by a compressor and expander turbine, in a simplification by a temperature–entropy diagram, a piston can be used to represent the mean compression and expansion. Further, magnetization $M$ can be considered as being analogous to volume $V$, and the magnetic field $H$ as analogous to pressure $p$.

1.3. Journey through the History of Magnetocalorics

The speed at which we live our lives in the present century is not favorable to the study of past scientific achievements. Sometimes, researchers describe present research and development as a “new twist,” without realizing that a certain idea, concept, experiment, or study is actually many years before. It is therefore crucial to present a chronological account of historical research, developments, and publications with the support of earlier and sometimes forgotten works.

The first indication of the discovery of thermomagnetic phenomena dates back to 1600, when Gilbert[109] experimentally discovered the reduced magnetization of an iron wire when it was heated. In 1843, Joule[110] discussed the “calorific effects of magneto-electricity,” although it is unclear whether this involved the heating of the sample and whether the observation was due to hysteresis or potential magnetocaloric effect, both being unknown at the time. A few years later, specifically in 1846, Faraday[111] referred to the decrease in magnetization with increasing temperature as being well known and described the phenomenon for different magnetic materials. Ideas for using the change in a material’s magnetization for power generation were first announced in 1879 by Houston and Thomson, who wrote an article titled “A curious thermo-magnetic motor.”[112] Only 2 years later, in 1881, Warburg[113] published a work in which he explained magnetic hysteresis. A year later, in 1883, Ewing[114] reported the same phenomenon and was the first to use the term “hysteresis” to describe it. In 1884, another
thermodynamic device was reported by McGee,[115] who designed a thermomagnetic wheel fabricated from iron wire and heated by Bunsen burners. At the end of the 1880s, several well-known scientists investigated the potential of thermomagnetic power generation. Several publications on thermomagnetic motors and generators were published by Edison[116] and Hering[117] in 1887. Edison later patented his ideas of the “pyro-magnetic” motor[118] and generator[119] while Tesla also patented his versions of the “thermo-magnetic” motor[120] and “pyromagneto-electric” generator.[121] It is, however, not well known that at the same time, another scientist, Stefan, explained the operation of a thermomagnetic motor, which exploited the transition between the ferromagnetic and paramagnetic states of a material.[122] Around the same time, other inventors acquired patents in the field of thermomagnetics.[123,124] In 1895, Curie[125,126] discovered the relationship between the change in the magnetization and the temperature of a material, referred to today as the Curie point.[126,127] However, there have been suggestions that this discovery was actually made by the French physicist Pouillet in 1832.[127,128]

Despite the rapid developments of the late 19th century, it was not until two decades later that the very important works of Weiss and Piccard was published in 1917[129] and 1918.[130] These researchers discovered heating of a nickel sample near its Curie temperature under an applied magnetic field change. They noted that the effect was reversible. Moreover, they also distinguished between this effect and the heating caused by hysteresis. The discovery was referred to as the “novel magneticocaloric phenomenon.” A decade later in 1926, Debye[131] and Giauque[132] independently discussed the adiabatic demagnetization of paramagnetic salts and its ability to produce sub-Kelvin cooling. Later in 1933, Giauque and MacDougall[133] demonstrated the adiabatic demagnetization of the paramagnetic salt Gd₂(SO₄)₃·8H₂O.[133] The work still represents the basis for the well-established use of adiabatic demagnetization for sub-Kelvin and cryogenic cooling. It is noteworthy, however, that there were other researchers who almost simultaneously made important contributions to the field, such as de Hass et al.[134] and Kürti and Simon.[135] In 1935, Urbain et al.[136] discovered ferromagnetism in gadolinium (Gd), which is the first magneticocaloric material determined to have a Curie temperature close to room temperature. Over the next 15 years, works on the utilization of magneticocaloric materials were within the area of low-temperature physics,[137,138] wherein the technology was used for magnetic cooling[139,140] well below 1 K.

The idea of thermomagnetic power generation was first revisited in 1948 by Brillouin and Iskenderian, who evaluated the design of a static thermomagnetic device for the direct conversion of heat into electricity.[141] In 1952, Chilowsky patented his ideas of a static thermomagnetic generator and refrigerator.[142] A few years later, in 1959, Elliott proposed a model similar to that of Brillouin and Iskenderian, in which Gd was used as the shunt material.[143] In the 1960s, researchers mostly investigated magnetocaloric power generation using magnetocaloric fluids, which can be traced to the important works of Resler Jr. and Rosensweig in 1964[144] and 1967,[145] respectively, and Voort in 1969.[146] After this time, there was only one publication related to magnetocaloric power generation, namely, by Bell and Braidsford in 1964, who investigated the thermomagnetic wheel.[147]

During the same time that magnetocaloric power generation was gaining research interest in the 1960s, adiabatic demagnetization lost its superiority in cryogenics, especially for when the dilution refrigeration temperature reached the milli-Kelvin level.[148,149] In 1972, an unusual experimental study on a thermomagnetic wheel with permanent magnets was conducted by Murakami and Nemoto.[150] The topic was again revisited in the 1980s, with several researchers showing interest in it. For example, magnetocaloric power generation using static solid working materials was investigated in 1984 by Kirol and Mills,[151] and in 1988 by Solomon.[152] Thermomagnetic power generation through mechanical motion was also investigated in 1989 by Solomon.[153]

The late 1970s and the 1980s were also a special period for magnetic refrigeration and heat pumping. In 1976, Brown demonstrated that Gd could be used as a refrigerant for magnetic refrigeration.[154] He fabricated and experimentally verified the operation of the first-ever prototype of a magnetic refrigeration system operating near room temperature. The device consisted of a 7 T superconducting coil with a linear-motion magnetocaloric regenerator with Gd plates. Two years later, Steyerl[155] published his work on the analysis of a rotary Stirling magnetic refrigeration cycle executed near room temperature. The use of heat regenerators in a magnetic refrigerator had been previously introduced in connection with magnetocaloric power generation in the 1960s, by researchers such as Resler Jr. and Rosensweig.[144] However, it was in 1982 that Barclay and Steyerl patented the idea of active magnetic regeneration (AMR),[156] which later became part of the processes of almost all prototype magnetocaloric refrigeration and heat pumping systems. In 1983, Rosensweig published a book on ferrohydrodynamics,[157] which included a comprehensive description of the thermodynamics and fluid dynamics of magnetocaloric fluids and the application of the fluids to magnetocaloric power generation. The first prototype of a rotary magnetic heat pump system was designed and fabricated in 1988 by Kirol and Dacus.[158] The heat pump included a stationary Nd-Fe-B permanent magnet assembly and four high field (0.9 T) areas and parallel Gd plates. Two years later, Green et al.[159] reported the development of a reciprocating magnetocaloric refrigerator that utilized two different magnetocaloric materials (Gd and Gd-Tb), a 7 T superconducting coil, and N₂ as the working fluid. In the late 1990s, Zimm et al.[160] developed another prototype reciprocating magnetic refrigeration system that utilized two active magnetic regenerators (AMRs) filled with Gd spheres, a 5 T superconducting magnet, and water as the working fluid.

The early prototypes of magnetic refrigeration systems were very robust. The use of superconducting magnets, which produced very strong magnetic fields, resulted in high energy efficiency. An increase in the change in the magnetic field increased the magnetocaloric effect, and hence the performance of the magnetic refrigerator (see the study by Kitanova et al.[130]). For instance, Zimm et al.[161] achieved a second-law efficiency of 30–50% for a non-optimized active magnetic regenerator and superconducting refrigeration system for a magnetic field change of 5 T.

The historical development of magnetocaloric energy conversion reveals that most of the researchers who undertook magnetocaloric power generation did not consider refrigeration,
and vice versa. In addition, despite the amount of studies that was conducted on magnetocaloric materials and energy conversion, the number of publications on the application of the technologies is rather small. This, however, changed in the 1990s, following an important milestone, namely, the discovery of the giant magnetocaloric effect by Pecharsky and Gschneidner.\[162\]

2. Magnetocaloric Refrigeration and Heat Pumping

A typical magnetocaloric refrigerator utilizes a magnetocaloric material in the form of the regenerator’s matrix. The heat transfer fluid, usually water containing inhibitors, oscillates through the regenerator in synchrony with the periodic magnetization/demagnetization, which is produced by the magnetic field source. The fluid oscillation is enabled by a hydraulic pump, which also connects the regeneration matrix with the external heat source and the heat sink heat exchangers. The most comprehensive description of the system and its thermodynamics and operation under different configurations using different parts can be found in the work of Kitanovski et al.\[35\] In this section, we provide up-to-date information on the related research and development of each part (Figure 4) of a magnetocaloric refrigerator and heat pump, as well as the operating principle and a review of the prototype systems that have been reported over the last 20 years. A note on the coefficient of the performance and the second law efficiency can be found in the Supporting Information.

2.1. Applied Magnetocaloric Materials

The magnetocaloric material is the heart of a magnetocaloric device. Magnetocaloric materials are of two types based on the order of the phase transition between the ferromagnetic and paramagnetic states, namely, first-order magnetocaloric (FOMT) materials, which undergo discontinuous change in magnetization with changing temperature, and second-order magnetocaloric (SOMT) materials, which undergo continuous change in magnetization with changing temperature.\[17,108,163\]

The most recent and most comprehensive review of magnetocaloric materials can be found in the work of Franco et al.\[36\] Another very important article on the material selection criteria was recently published by Gottschall et al.\[37\] The latest review of manganese-based magnetocaloric materials was presented by Chaudhary et al.,\[164\] while another interesting publication was authored by Lyubina.\[165\] who reviewed magnetocaloric materials with an adiabatic temperature change rate of higher than 2 K T–1. Some older reviews are also available in the literature.\[106,163,166,167\]

Generally, both FOMT and SOMT materials are used for magnetic refrigeration and heat pumping.\[35,168\] Gd is a conventional and reference SOMT material with a Curie point close to room temperature, and its alloys with rare earth metals (e.g., Tb, Er, and Dy) are other examples. Conventional FOMT materials include La-Fe-Si-H,\[169–171\] La-Fe-Mn-Si-H,\[172–174\] La-Fe-Co-Si,\[175–177\] and Mn-Fe-P-Si.\[178–180\]

Why are these materials more interesting for application in real magnetic refrigeration and heat pumping systems?

Figure 4. Overview of different configurations of a magnetocaloric refrigerator or heat pump and characterization of the operating principle (EM, electromagnet; EPM, electro-permanent magnet; MCM, magnetocaloric material; MC reg., magnetocaloric regenerator; PM, permanent magnet assembly; SCM, superconducting magnet).
Although it is clear that magnetocaloric materials that exhibit a large magnetocaloric effect are more suitable for refrigeration and heat pumping, it is not similarly recognized that the most important feature of the magnetocaloric effect is a large adiabatic temperature change. Also of secondary importance is the isothermal entropy change, which is often mentioned in related works. The isothermal entropy change is an indication of the cooling capacity of a magnetocaloric refrigerant. However, it does not provide information on whether the material is usable for a refrigeration device, because heat cannot be transferred isothermally. The adiabatic temperature change provides a basis for establishing the temperature gradient of a magnetocaloric material. Moreover, considering that the heat transfer between the material and the working fluid is irreversible, a large adiabatic temperature change is required to overcome the irreversible heat losses. However, this must not be achieved at the expense of the cost effectiveness of the magnetic field source. This is the reason why Lyubina focused on magnetocaloric materials with adiabatic temperature change rates of higher than 2 K T−1. A high adiabatic temperature change is required because the heat transfer from or to a magnetocaloric material is irreversible and the convective heat flux is limited by the temperature difference between the material and the working fluid. Consequently, if the magnetocaloric material exhibits a high entropy change but a small adiabatic temperature change, it may only be usable for cooling using a specific heat source, but not for the establishment of a temperature gradient such as is required for refrigeration and heat pumping. The adiabatic temperature change and the isothermal entropy change of the magnetocaloric material should be correctly indicated under the cycling conditions and realistic conditions for any refrigeration or heat pumping system. This important fact actually concerns hysteretic materials and was excellently addressed in a recent publication by Gottschall et al. This is also the reason why low-cost and rare-earth-free Heusler alloys, despite having been the focus of intensive research, are currently not being considered for the development of magnetic refrigeration and heat pumping systems, except there are relevant new findings.

Knowing that the magnetocaloric effect causes a large adiabatic temperature change for the smallest possible magnetic field change, which is mostly associated with the cost of the field source, it is important to also consider the environmental, resource, and geopolitical issues associated with the practical application of specific magnetocaloric materials.

The mass production of the raw materials used for the development of magnetic refrigeration systems was investigated by Gauß et al. including the critical effects of the demand-supply factors of magnetocaloric materials. The authors identified Gd-based materials as being critical in this regard, while La-Fe-Si-based and Mn-Fe-P-based magnetocaloric materials are substantially less problematic. Gottschall et al. recently drew similar conclusions, making a critical assessment of magnetocaloric compounds with respect to their geological availability, geopolitical factors, recyclability, and sustainability, highlighting the heavy rare-earth Gd as very critical and impractical for large-scale utilization. Therefore, Gd and its alloys are not likely to be adopted as solid refrigerants in future everyday refrigerators, but could be used for reference experimental investigations. The Ni-Mn-In-(Co) Heusler alloys are considered as being of medium-to-high risk based on their In and Co contents. Because these alloys are also problematic with regard to their cyclic magnetocaloric properties, it is not likely that they would be utilized in future magnetocaloric devices, although they cannot be entirely disregarded. Magnetocaloric materials of the La-Fe-Si-Co group are considered to be of medium-to-low risk owing to their small Co content, while those of the La-Fe-Si-X-H group are of low risk because La is the least critical of the rare-earth elements, occurring relatively more abundantly. A low risk is also associated with the Mn-Fe-P-Si materials.

Research is ongoing to find new candidate materials. One of the most comprehensive searches for new magnetocaloric compounds was conducted by Bocarsly et al. who screened 134 ferromagnetic materials and an additional 30 compounds to assess their potential as magnetocaloric application. However, the most recent and most comprehensive search involved the assessment of more than 1000 materials, among which the 10 best were selected for further experimental evaluation.

The hysteresis of magnetocaloric materials is another problem requiring solution and recent years have witnessed several publications on the subject. Although most of these works considered Heusler alloys, it is important to mention other important and more applicable FOMT materials. An investigation of the thermal hysteresis of different magnetocaloric materials such as La-Fe-Si-based, Heusler-based, and Fe2P-based compounds was performed by Gutfleisch et al. The work included an examination of the causes of the hysteresis and possible methods for reducing it. Another comprehensive study was conducted by Scheibel et al. who investigated the origin of the large magnetocaloric effect and hysteresis of several first-order magnetocaloric materials such as Ni-Mn-based Heusler alloys, FeRh, La(FeSi)13-based compounds, Mn3GaC anti-perovskites, and Fe3P compounds.

Another problem associated with magnetocaloric materials is their effect on the environment. Although these materials have an ozone depletion potential and global warming potential of zero, these parameters are not the only environmental criteria for screening refrigerants. Also taken into consideration is the entire life cycle of the refrigerant, from production to use and eventual disposal. The total equivalent warming impact (TEWI), which incorporates direct and indirect emissions, is another important criteria. However, a more comprehensive but yet to be investigated criteria is the Life Cycle Climate Performance (LCCP), which represents the sum of the full direct emissions (annual leakage and leakage during the disposal of the unit) and indirect emissions (manufacturing process, energy consumption, and disposal) associated with the lifetime of the system. Aprea et al. numerically investigated and compared the TEWIs of different FOMT and SOMT refrigerants. They showed that GdSi2Ge2 and LaFe11.384Mn0.356Si1.26H1.52 had TEWIs that were always lower than that of a vapor-compression plant. Furthermore, they showed that the TEWI of an AMR cycle using a FOMT material was always better than that of one using a SOMT material. In 2018, the study was extended to consider other caloric materials. The recycling of rare-earth elements was also investigated in the comprehensive study of Tunsu and Petranikova. This study also considered the use of hydrometallurgy for the recovery of rare earth metals from...
commercial magnetocaloric materials containing Ce, Fe, La, Mn, and Si.

There remains the question of establishing a useful figure of merit for magnetocaloric materials. In this regard, there is an ongoing debate among researchers about which parameters to take into consideration. For example, in the recent publications of Niknia et al. and Griffith et al., who investigated different figures of merit for their potential use as indicators of the refrigeration capability of a magnetocaloric material. In vapor-compression refrigeration, the refrigerant's capacity is defined by the enthalpy change that occurs during the evaporation (or cooling process). In analogy with conventional refrigeration, the most correct way to characterize the capacity of a refrigerant is connected with the process of the isothermal entropy change that occurs at a certain temperature. Therefore, regardless of the process (cascade system, regeneration), this can simply be expressed by the following expression: $q = T \times \Delta S$, where $T$ (K) is the temperature at which the capacity is defined, and $\Delta S$ (J kg$^{-1}$ K$^{-1}$) is the total isothermal entropy change of the magnetocaloric material. On this basis, it is possible to establish the area of the refrigeration capacity for any magnetocaloric material and magnetic field change. This was well demonstrated in the recent publication of Gottschall et al. However, whereas the ideal refrigeration capacity is an important figure of merit of the cooling capability of a magnetocaloric material, it does not provide information about the adiabatic temperature change, which is crucial to the regeneration and potential temperature span of a real magnetocaloric refrigerator or heat pump. Here, we refer to the work of Niknia et al. The figure of merit related to the cooling capacity of a magnetocaloric material, which performs reversible work between defined upper and lower magnetic fields (i.e., the Carnot cycle) during refrigeration or heat pumping, strongly depends on both the adiabatic temperature change and the isothermal entropy change. As in Niknia et al., this can be simply expressed as $w = \Delta T_{ad} \times \Delta S$, which is the maximum adiabatic temperature change times the maximum isothermal entropy change. Alternatively, it can be related to the temperature and the corresponding adiabatic temperature and isothermal entropy changes, which would give the temperature-dependent area of $w$.

Based on a review of previous works in materials science and engineering, the most important requirements for a magnetocaloric material can be presented as shown in Figure 5.

Future research and development of magnetocaloric materials should focus on four main groups of non-critical materials, namely, some manganites, Heusler alloys, La-Fe-Si-H materials, and Mn-Fe-P-Si-based materials. In addition to the criticality and toxicity of the material, the cyclic adiabatic temperature change is the most important selection criteria. Although La-Fe-Si-H and Mn-Fe-P-Si materials satisfy the criteria in Figure 5 to some extent, there is the need to invest more effort in solving the hysteresis problem and substantially improve the cyclic adiabatic temperature change of manganites and Heusler alloys. Otherwise, materials of these two groups would not be usable for magnetocaloric refrigeration or heat pumping. Moreover, there is the need to increase the very low thermal conductivity of manganites.

An understanding of the magnetic phase transitions also provides a good basis for tailoring and improving the performance of magnetocaloric materials. More research effort should be directed at obtaining fine, preferably single-crystal particles with a uniform size. Another important issue worthy of future research is the use of nanoengineering methods to achieve improvements such as broadening of the magnetocaloric effect and strengthening its intensity. This may not be effective for FOMT materials but would be a useful tool for tailoring manganites. Nanostructuring of Gd-Ti into multilayers has been used to enhance the magnetic field responsiveness, and this may be also interesting for other types of materials. Much effort has likewise been invested in minimizing the hysteresis and improving the magnetocaloric effect of Heusler alloys over the last few years. The mastering of hysteresis requires a very good knowledge of its intrinsic and extrinsic origins, supported by theoretical and experimental investigations toward tailoring the material with a reversible magnetocaloric effect.

An important issue in this regard is the tuning of the magnetocaloric material to obtain a large magnetocaloric effect over a broad temperature span. For instance, Dung et al.
demonstrated that a broad range of Mn-Fe-P-Si materials with different Curie temperatures can be obtained by varying the composition on the magnetic sublattices. They also achieved a significant reduction of the thermal hysteresis. The fine-tuning of the Curie temperature by varying the Mn concentration of hydrogenated La(Fe-Mn-Si)13-H compounds was reported by Basso et al.\cite{173} The tuning of Heusler alloys can also be achieved by varying the composition\cite{186,35} or the microstructures of thin films, which strongly impact the phase transformation temperature.\cite{36} If the tuning of a magnetocaloric material belonging to a certain group fails to broaden the temperature span, materials from different groups can still be used to produce the magnetocaloric regenerators.

There are three other issues that also require solution to obtain the best FOMT (La-Fe-Mn-Si and Mn-Fe-P-Si) materials for practical applications. They are 1) cyclic stability (ability to withstand $10^8$ cycles), 2) manufacturability (solving the proneness to cracking during machining) and processing into fine structures, and 3) increasing the low thermal conductivity. As would be discussed later in connection with the processing of magnetocaloric regenerators, the brittleness of FOMT materials can be addressed by polymer\cite{206,207} or metal\cite{208,209} bonding. Bonding also facilitates the processing of FOMT powders into desired shapes, such as by hot pressing or extrusion. In the case of the bonding of a polymer, which remains in the structure after the processing, the problem is the resultant lower thermal conductivity and the sensitivity of the mechanical properties of the polymer to fatigue and aging.\cite{210} Moreover, there is the need to minimize the thermal mass of the epoxy material used as a binder because it influences the effective magnetocaloric effect of the regenerator. One means of doing this is to extract the polymer (resin) after forming the regenerator,\cite{211} although this may also affect the mechanical stability of the structure. Further investigation is, thus, required in this direction. Regarding improvement of the mechanical stability, the introduction of porosity has been proposed.\cite{212} However, because porosity decreases the thermal conductivity, Lyubina et al.\cite{213} employed the introduction of Cu through electroless plating, with the resultant magnetocaloric composite exhibiting substantially improved thermal conductivity and mechanical stability with only a small reduction in the magnetocaloric effect. There is, thus, also the need for further study toward achieving magnetocaloric materials with very fine, layered structures, such as was attempted by powder-in-tube (PIT) technology in a recent study,\cite{214} in which cladded La(Fe, Co, Si)13 powder with a thin seamless austenitic steel jacket was employed. This method could be explored for use in achieving different shapes, cyclic stability states, and layered and finer structures.

The thermally induced decomposition and recombination process of La-Fe-Si materials was established a decade ago. The process enables the machining and subsequent hydrogenation of the base material\cite{215} and is now currently applied as part of a large-scale production of magnetocaloric materials by the German company Vacuumschmelze.\cite{216} The production of magnetocaloric materials in this company involves the following steps, which are based on powder metallurgy, vacuum induction melting and casting, crushing and milling, and die or isostatic pressing of the semi-finished blocks. This is followed by machining and surface finishing into the desired shape. Finally, hydrogenation is performed.

As the search for other useful methods continues, including for large-scale production, gas atomization holds some promise as a very rapid solidification process. This efficient and easily scalable method for producing powder with spherical particles of varying sizes\cite{217} can be effectively combined with powder extrusion\cite{211} or PIT technology.\cite{214} On the other hand, additive manufacturing methods enable the tailoring of increasingly finer and sophisticated structures and the application to different magnetocaloric materials.\cite{218–220} Future research in this area should focus on improvement of the mechanical properties, layering, and effective process control toward achieving strong but very fine architectures. There is the possibility that this technology would eventually represent the basis for the mass production of magnetocaloric refrigerants.

### 2.2. Active Magnetic Regenerators

The magnetocaloric effect of a magnetocaloric material is not sufficient for achieving the temperature span required for magnetocaloric refrigeration and heat pumping devices. It is, however, used in low-temperature physics for adiabatic demagnetization refrigeration, in which paramagnetic salts are cooled to milli-Kelvin temperatures. Because this subject will still be discussed later in the article, the primary focus here will be near-room-temperature applications.

There are two options available for increasing the temperature span of the magnetocaloric effect. The first utilizes a cascade system consisting of several interconnected thermodynamic cycles,\cite{35,221} while the second involves heat regeneration. In some technologies, a heat regenerator consists of an indirect heat exchanger in which the heat exchange occurs by means of convective heat transfer through a fluid that is periodically stored or transferred from or to the regenerator material (i.e., the regenerator matrix). The regenerator matrix is, thus, a porous structure through which the working fluid oscillates.

One of the most basic examples can be found in the Stirling engine\cite{222} invented by Robert Stirling in the early 19th century. If the porous matrix is a magnetocaloric material, it is said to be active, because it not only absorbs or transfers heat, it also actively contributes to the magnetocaloric effect. Hence, the regenerator is referred to as an AMR.\cite{156}

Because most magnetocaloric prototype refrigerators and heat pumps operate on the AMR principle, special attention would be given to the processing of regenerators, their layering with different magnetocaloric materials, and optimization of their performance and geometry.

### 2.3. Processing of Regenerators

A magnetocaloric regenerator must have a very large heat transfer surface to provide efficient convective heat transfer from or to the working fluid. The convective heat transfer is strongly dependent on the scale of the heat transferred between a particular body and the working fluid. This can be demonstrated
for the macroscopic effect by the simple relationships of the dimensionless Nusselt number, which is linearly related with the heat transfer coefficient and the thermal conductivity of the fluid, respectively, and inversely related with the characteristic length of the particular fluid void or channel. These are well-known relationships that can be found in every book on convective heat transfer.\(^{223,224}\) The porosity of the regenerator therefore strongly depends not only on the properties of the magnetocaloric material, but also on the viscosity and thermal properties of the working fluid and the fluid dynamics. When a gas is used as the working fluid, the porosity should be relatively high. When a liquid such as water containing anti-corrosion and/or anti-freeze inhibitors is used, the porosity of the regenerator is 35–45%\(^{,135}\) Other important issues regarding a magnetocaloric regenerator and its materials are manufacturability and mechanical (cyclic) stability. This is especially important when the regenerator utilizes FOMT materials that exhibit volume change through magnetostriction. With regard to their shape, magnetocaloric regenerators can be divided into two types, namely, those with packed-bed structures and ordered structures, respectively (Figure 6).

For instance, the magnetocaloric regenerator that was used in the first room-temperature magnetic refrigerator consisted of an ordered structure with parallel plates of Gd.\(^{,154}\) According to a review of the processing techniques for AMRs until 2015 presented by Kitanovski et al.,\(^{,156}\) the previous 5 years had witnessed progress with different approaches to processing magnetocaloric regenerators. These approaches are described in chronological order below with reference to the works of the relevant researchers around the world.

Cold processing by wire-saw cutting and cold rolling into thin polymer-bonded La(Fe,Mn,Si)\(_{13}\)H\(_x\) plates was performed by Radulov et al. in 2015.\(^{,206}\) The authors investigated the magnetocaloric properties and corrosive behavior of the material over a period of 7 months to evaluate the practicality of the device. An attempt to produce magnetocaloric wires from Heusler alloys was also reported by Varga et al. in 2015.\(^{,225}\) They successfully produced glass-coated NiMnGa- and NiMnInCo-based microwires. Further, Taskaev et al.\(^{,226}\) conducted a study in which the well machinable and representative magnetocaloric material Gd was used as the reference material. They showed that severe plastic deformation dramatically changed the thermodynamic properties of Gd, resulting in a significant decrease in the specific heat around the Curie temperature. They also presented the appropriate annealing conditions for restoring the magnetocaloric properties of previously cold-rolled Gd. A hot pressing study was conducted by Liu et al.,\(^{,209}\) who bonded Cu with a La-Fe alloy. In 2016, Karpenkov et al.\(^{,227}\) considered two methods for processing the Y\(_2\)Fe\(_{17}\) ribbons into regenerators, forming stacked 100 µm-thick plates with 100 µm fluid channels. In the first method, the rapidly quenched ribbons were glued by applying thermally conductive epoxy. In the second method, the stacked ribbons were sintered at a temperature of 30 K below the melting point of the Y\(_2\)Fe\(_{17}\) phase. In the same year, Kondo et al.\(^{,228}\) experimentally validated the feasibility of processing Gd into 0.25 mm wires. They experimentally examined the corrosion behavior and operation of the regenerators using twisted and straight wires, respectively. In the 2017, Bahl et al.\(^{,229}\) processed and experimentally validated the magnetocaloric properties and AMR performance of hot-pressed bonded plates fabricated from La\(_{0.85}\)Ce\(_{0.15}\)Fe\(_{11.25}\)Mn\(_{0.25}\)Si\(_{1.5}\)H\(_x\) particles and resin. The authors reported a volume ratio of magnetocaloric material in the plates of 0.53, which is due to the 5 wt% of resin and porosity. A regenerator produced from metal-bonded La(Fe,Mn,Si)\(_{13}\)H\(_x\) powder was experimentally examined by Radulov et al.\(^{,208}\) The authors emphasized that the metal coating of the magnetocaloric particles significantly contributed to the corrosion resistance and mechanical and cyclic stability. The main disadvantage was that the arbitrary shape of the La(Fe,Mn,Si)\(_{13}\)H\(_x\) particles affected the channel structure by blinding or closing the voids for the fluid flow. The same authors\(^{,210}\) conducted a similar study in which the magnetocaloric powder was processed using Field’s alloy binders. Another study that considered metal binding was conducted by Wenkai et al.\(^{,210}\) The authors hot pressed La-Fe-Si-H using indium as the binding material to form 0.8 mm-thick plates. Indium was chosen because of its low melting point and relatively high thermal conductivity. An adiabatic temperature change of 5.88 K was reported for a magnetic field change of 2 T. To address the brittleness and relatively low thermal conductivity of La-Fe-Si-H alloys, Shao et al.\(^{,231}\) processed blocks and plates of the alloys by adding extra α-Fe as a reinforcement phase to enhance the mechanical integrity. The authors reported a thermal conductivity of 6 W mK\(^{-1}\) and reproducible Δ\(_{\text{ad}}\) of 5.4 K for a magnetic field change of 1.93 T. They also applied a method for processing magnetocaloric regenerators via metallic additive manufacturing. The method was implemented by Shamba et al.\(^{,232}\) who processed LaFe\(_{11.8}\)Si\(_{1.4}\) alloys using spark plasma sintering. A comprehensive experimental study on the use of Gd was performed by Trevizoli et al.\(^{,233}\) In the first part of the study, the authors fabricated stainless-steel regenerator samples with different geometries: parallel plate, pin array, and sphere-packed bed. After testing these samples, they also designed and fabricated the corresponding Gd regenerators. Wieland

![Figure 6. Types of magnetocaloric regenerators.](Image)
and Petzoldt[211] powder-extruded and sintered a La-Fe-Mn-Si alloy and fabricated a very well-ordered parallel-channel structure with a wall thickness of <300 μm. Funk et al.[214] also conducted a very important study on the PIT processing of La compounds in a steel jacket tube. The obtained La-based and Mn-based FOMT materials exhibited substantially improved mechanical and chemical stability when used to fabricate regenerators. Lei et al.[207] also fabricated a five-layer regenerator from epoxy-bonded La(Fe,Mn,SI)$_3$H$_y$ particles. In addition, a numerical analysis of twin-wedge wires was recently performed by You et al.[214] while Sheng et al.[239] conducted a comprehensive experimental study, based on which they designed various Gd$_{20}$Ho$_{20}$Er$_{20}$Al$_{20}$TM$_{20}$ (TM = Fe, Co, and Ni) microwires with different diameters. The smallest microwire had a diameter of <60 μm and length of a few meters.

2.4. Numerical Simulations and Experiments on Active Magnetic Regenerators

Because the magnetocaloric effect is limited by the temperature interval in which it occurs, it is more effective to operate a magnetocaloric refrigerator or heat pump as a layered regenerator using multiple magnetocaloric materials. Thus, in the steady state, each material layer of the regenerator operates at the temperature that maximizes its magnetocaloric effect. Such layering of magnetocaloric materials with differing Curie temperatures had been previously proposed by the inventors of the active magnetic regenerator in 1982.[156] The layering is especially important for first-order materials, which have a rather narrow magnetocaloric temperature range. We will now discuss some numerical and experimental investigations of both single-layered and multi-layered magnetocaloric regenerators, a research domain that is one of the most active in the field of magnetocalorics. Indeed, a vast number of studies have been conducted in this area and we will only attempt a brief review of the most important ones until 2014, and then take a more detailed look at the research and developments over the past 5 years.

In 2004, Richard et al.[216] reported their work on single-layered and two-layered packed-bed regenerators. The two regenerators had similar masses and dimensions, with the single-layered one fabricated using only Gd, and the two-layered one having a Gd layer and Gd-Tb layer. The study results revealed that the two-layered regenerator produced a higher cooling power and had a broader temperature span. In 2006, Rowe and Tura.[227] experimentally investigated three-layered regenerators with different combinations of Gd, G-Tb, and Gd-Er. Helium gas was used as the heat transfer fluid, resulting in a rather wide no-load temperature span of 50 K. The authors concluded that the layering did not always enhance the performance and that the optimal quantities of the different materials depended on the load and operating temperature. In 2011, Aprea et al.[238] numerically analyzed layered regenerators fabricated from Gd-Tb and Gd-Dy alloys, and showed that layered bed regenerators significantly outperformed single-material regenerators. The most comprehensive review study of numerical models of magnetocaloric refrigeration and heat pumping systems used until 2011 was conducted by Nielsen et al.[239]. In 2013, Engelbrecht et al.[240] improved previous numerical simulation models of active magnetic regeneration and compared the predictions of the new model with experimental results. They importantly concluded that both numerical modeling and experimental implementation required carefulness regarding the effects of demagnetization, fluid flow maldistribution, and heat gains or losses. Another important study was performed by Burdyny et al.[241] who developed a special simplified modeling framework for analyzing active magnetic regenerators based on the work of Rowe.[242,243] Comparison of their numerical results with experimental data revealed relatively good agreement. In 2014, Tušek et al.[244] experimentally compared seven-, four-, and two-layered active La-Fe-Co-Si magnetic regenerators and a simple Gd regenerator, and found that using several layers did not necessarily improve the performance. Plaznik et al.[245] and Kitanovski et al.[246] also performed interesting studies that considered different thermodynamic cycles and the active magnetic regeneration principle. The different cycles were experimentally and numerically evaluated and compared, and it was found that the typical Brayton-like and Ericsson-like cycles did not produce the best performance, and the use of Carnot-like cycles was expensive. Kitanovski et al.[35] presented the most comprehensive review of numerical and experimental investigations of active magnetic regeneration until the time of their publication in 2015. Considering the many studies that have been conducted on both single- and multi-layered active magnetic regenerators since this review, we will look at the most outstanding ones, especially the experimental works.

In 2015, Chiba et al.[47] reported experiments performed using different fractions of La-Fe-Co-Si compounds based on their Curie temperature between 275 and 315 K. Because the materials were not layered in the direction of the temperature gradient, a small change in the adiabatic temperature of the structure was observed. However, this occurred over a wide operating temperature span. A subsequent publication in 2017[248] reported on additional numerical and experimental investigations of two parallel-plate active magnetic regenerators fabricated using four La-Fe-Co-Si compounds with different Curie temperatures. In addition to the validation of the numerical model, the authors highlighted problems related to hydraulic losses as one of the important issues requiring further attention. In 2015, Torregrosa-Jaime et al.[249] proposed a new finite-difference model that optimally combined explicit and implicit techniques for solving 1D transient heat transfer in an active magnetic regenerator. The model substantially reduced the calculation time compared with previous similar models. A comprehensive study of the effect of layering on the performance of an AMR was conducted by Teyber et al.[250] They performed numerical simulations and experiments using four regenerator configurations consisting of different layers of magnetocaloric materials. The first method for the optimization of the number of layers of an active magnetic regenerator was presented by Tomc in 2016.[45] The method involves the use of neural networks to determine the optimal number of layers for any magnetocaloric material. The model was experimentally verified using different parallel-plate regenerators consisting of layers of La-Fe-Co-Si compounds. It was found that, for given operating parameters, there was a finite number of
layers that could be used and an optimal length of each layer. A comprehensive numerical and experimental assessment of a packed-bed Gd-based active magnetic regenerator was performed by Trevizoli et al.\cite{252,253} The regenerator was exposed to a rectified sinusoidal magnetic flux in phase with a sinusoidal fluid flow waveform. It was concluded from the results that further work was required for improvement of the modeling of active magnetic regeneration, and its evaluation. In addition to consideration of the internal irreversible heat transfer and viscous losses, there was the need to incorporate the demagnetizing losses and heat losses and also consider the presence of dead volumes between each end of the regenerator and the external (heat source and heat sink) heat exchangers. In 2017, Govindappa et al.\cite{254} conducted an experimental investigation of active magnetic regenerators fabricated from MnFeP$_{1-x}$As$_x$. They produced five different matrices, with one composed of three layers, another of six layers, and three of eight layers of the magnetocaloric materials. The lengths of the layers were varied. It was found that too many layers caused mismatch of the operating temperature range of the regenerator. Dall'Olio et al.\cite{255} conducted a numerical study on the layering of a regenerator with 10 layers, including the use of a variable cross section (tapering) along the length of the regenerator. They found that the tapering enabled better air gap utilization compared with a straight bed regenerator, and also reduced the cost of the magnet. However, this was accompanied by significant reduction of the heating power. Zhang et al.\cite{256} used numerical simulation to investigate the case of the highest number of layers (16) that had so far been reported for an active magnetic regenerator fabricated from La-Fe-Mn-Si-H compounds. A set of 137 simulations using different magnetocaloric material specifications was used to optimize the layer–length distribution of the regenerator. The performance of the regenerator was evaluated at different frequencies and using different fluid flows. The results revealed that the 16-layer active magnetic regeneration system with a 41 K temperature span could operate at a low frequency of 0.1 Hz with 84% second-law efficiency for a magnetic field change between 0 and 1.5 T. These results were obtained for a water/glycol working fluid, which oscillated through the layered regenerator consisting of parallel plates of length 200 mm and thickness 0.75 mm. The total mass of each plate was determined to be 1.05 kg. The cooling power achieved at the high operating efficiency was <10 W. However, it is not clear how many plates were used in the regenerator. Lei et al. in 2017,\cite{257} numerically evaluated the performance of active magnetic regenerators fabricated from Gd with four different configurations, namely, parallel plates, circular micro-channel matrix, rectangular micro-channel matrix, and packed-screen bed. The parallel plates and micro-channel matrices were found to produce the highest theoretical efficiency, although the packed-screen and packed-sphere beds were probably more practical. The hydraulic behavior and carry-over losses of an active magnetic regenerator were investigated by Trevizoli and Barbosa in 2017. The thermal performance predictions of a numerical model of the regenerator were compared with a large experimental database for packed-bed regenerators composed of stainless steel spheres. Another numerical study was conducted by Aprea et al.\cite{259} in 2017, wherein simulations were performed using 2D models of active magnetic regenerators fabricated from six different magnetocaloric materials. The results of the study were verified by comparison with those of previous experimental investigations. An improvement based on extensive numerical and experimental studies was reported by the same research group in 2018.\cite{260} Teyber et al.\cite{261} achieved a record no-load temperature span of 40 K for an active magnetic regenerator using a magnetic field change of 1.45 T provided by a permanent magnet assembly. They also developed and experimentally verified an accurate semi-analytical model with a very short computation time. Another study on layered magnetocaloric regenerators was conducted by Christiaanse et al.,\cite{262} who experimentally evaluated the performance of six different regenerators with five different layers of Mn-Fe-Si-P compounds. They emphasized the benefit of layering magnetocaloric materials with smaller Curie temperature differences. They showed that larger Curie temperature differences (>10 K) between two neighboring layers caused independent operation of the latter, resulting in a substantially decreased performance of the active magnetic regenerator.

Mugica et al.\cite{263} developed an open-source direct numerical simulation solver that enabled simulation of active magnetic regeneration cycles. They showed that the model could be applied to regenerators with different geometries and properties, as well as to other caloric technologies. An interesting numerical study was also conducted by Monfared and Palm,\cite{264} who investigated and compared the performances of different layered AMRs with the purpose of determining the extent of magnetocaloric material improvement required for a magnetic refrigeration system to outperform a vapor compression system. The authors noted that, in addition to the requirement for uniformity of the transition temperature of each layer of magnetocaloric material, there was the need for a small increment in the transition temperature between adjacent layers, as well as cyclic stability of the materials. Further, there is the need for magnetocaloric materials that exhibit an adiabatic temperature change 2.35 times that of existing materials to outperform vapor compression systems. Some of the more significant problems of active magnetic regenerators are the mass imbalance related to the duration of the fluid flow and the need to synchronize the magnetic field and fluid flow. This was further investigated by Nakashima et al.,\cite{265,266} who examined the effects of the flow rate waveform and mass imbalance on the performance of an active magnetic regenerator with a Gd packed bed. Flow maldistribution in the regenerator was found to substantially affect the performance and could cause large irreversible losses. This problem is that of the well-known flow through porous or channeled bodies, or in the field of heat exchangers.\cite{267,268} This important issue was thoroughly investigated by other researchers.\cite{269,271} One of the last and most interesting studies on the subject was conducted by Navickaitė et al.\cite{272} who investigated the possibility of improving the geometry of an active magnetic regenerator using double corrugated tubes. Several numerical simulations were performed using this geometry and the same parameters (magnetic field change of 1.2 T, heat source at 275 K, heat sink at 300 K) and working fluid (water), but varying the Gd-based regenerator materials. The results showed that the proposed geometry was effective. The viscous losses were also found to
For similar hydraulic diameters, the packed beds have substantially higher viscous losses than ordered structures. Viscous losses can drastically decrease the efficiency of the device, since the large pumping power and the heat generation in the regenerator. Future designs should focus on ordered, micro-channel structures of active magnetic regenerators.

The fluid maldistribution can significantly affect the performance of the regenerator. It is not important only inside the structure, but also at the entrance and exit of the regenerator.

During the operation, the magnetostriction can affect the porosity (fluid voids) in the regenerator’s structure. This must be prevented.

The position of valves should be such, that their potential heat gains are executed from the system before the fluid enters the regenerator.

The dead volumes in the regenerator, including the space between the regenerator material and its inlet/exit compartment should be minimized.

The fluid flow rate waveform importantly influences the performance of the regenerator.

The layering of active magnetic regenerators is necessary for applications in refrigeration and heat pumping. The optimal number of layers is finite for given temperature span and frequency of the operation. The optimization requires advanced methods (i.e., neural networks).

The thermal storage in the magnetocaloric material (thermal mass imbalance), in the working fluid (carry-over due to varying magnetic field) and in the housing (carry-over due to varying magnetic field) can strongly decrease the performance of the active magnetic regenerator.

The demagnetization drastically decreases the performance of the active magnetic regenerator. The geometry with respect to the applied magnetic field must be formed accordingly.

![Figure 7. Tips for the design of energy-efficient active magnetic regenerators.](image)

2.5. Thermal Control Elements

Active magnetic regeneration is the thermodynamic cycle most utilized for magnetic refrigeration and heat pumping. However, the conventional active magnetic regeneration principle is not applicable to refrigeration, air conditioning, or heat pumping near room temperature using current magnetocaloric materials, that is, when a larger temperature span (e.g., >20 K) and high power density per mass of the device is required. This is not because of the confirmed high energy efficiency of the active magnetic regeneration cycle, but the very low power density under such conditions imposes strict limitations on the applicability. The same problem is encountered in other caloric technologies, except when the mass of the caloric material or cost of the device is unimportant. This is the main reason why conventional active magnetic regeneration is unlikely to find broad application in the future.

In practice, for a given temperature span and cooling power and the corresponding high second-law efficiency, the operation frequency should be a minimum of 5 Hz, preferably higher. The low likelihood of an active magnetic regeneration device simultaneously fulfilling all these conditions is evident from any of the relevant works already cited in this article.

This necessitates the adoption of another thermodynamic principle. Considering the small adiabatic temperature change of current magnetocaloric materials, it is clear that such a principle would inevitably require very efficient heat transfer, as well as regeneration or cascading. However, there is also the question of how to increase the frequency without also increasing the viscous losses, which adversely impacts the energy efficiency and basic operation of the device?

The last decade has witnessed a large amount of research in the field of thermal sciences, and this has resulted in the opening and revisiting of some thermal elements. The thermal elements are used to control the heat flux or thermal resistance on different size and time scales and are of four main types, namely, thermal switches, thermal diodes, thermal regulators, and thermal resistors. Conscientious research has led to new findings and substantially improved knowledge of the thermal sciences and transport phenomena, including on the macro-, micro-, and nano-scale. It is, therefore, not a coincidence that activities in the field of heat conduction have been characterized by the term “renaissance.” Some types of existing thermal switches are very commonly used in low-temperature physics, including for adiabatic (magnetocaloric) demagnetization processes. Although they are efficient for cryogenic applications, most of them are unsuitable for magnetocaloric refrigeration and heat pumping, which require change
of the heat flux direction at least 10 times per second. Beyond adiabatic demagnetization using magnetocaloric materials, the idea of using thermal control elements in caloric technologies was first directed at electrocalorics in 1988.\[679\] However, relevant research along this line only commenced two decades later, and in 2010, it was extended to magnetocalorics.\[282\] Between 2011 and 2012, a solid-state refrigerator with mechanically actuated thermal switches was developed and experimentally tested by Tsukamoto et al.\[283,284\] The use of a La-based alloy was found to produce a rather high ratio between the thermal resistances during the “off” and “on” operations, specifically a switching ratio of 22.5. However, the switching time was rather long at 5.5 s. Tasaki et al.\[285\] used the idealized heat transfer model for thermal switches to perform a simple numerical evaluation and achieved a potential cooling power density higher than that of active magnetic regeneration. A more comprehensive study conducted by Olsen et al.\[286\] revealed that the application of thermal switches could increase the cooling power to 3.5 times that of an active magnetic regenerative cycle under the same conditions. In 2012, Silva et al.\[287\] conducted a theoretical study that involved imaginary thermal switches with thermal resistances that were varied by an external magnetic field and a single-stage device without regeneration. This interesting study produced a potential maximum specific cooling power of 2.75 W cm$^{-2}$ for an operating heat sink temperature of 296 K under a magnetic field change of 1 T. A few years later, an upgraded numerical model for evaluating a cascade system was used to obtain larger temperature spans of 2.5–11.5 K.\[288\] The use of Peltier modules as thermal switches for magnetocaloric refrigeration has also been the subject of several studies. In 2013, Tomc et al.\[289\] performed extensive numerical simulations of micro-Peltier thermal switches with integrated magnetocaloric material. The Peltier modules were considered to be synchronized with the varying magnetic field; thus, alternately turning the modules “on” and “off” performed the thermal switching operation. The simulations showed that the Peltier modules could theoretically reach operating frequencies above 200 Hz with cooling power densities of 2–10 kW kg$^{-1}$ of magnetocaloric material. In a subsequent study, Tomc et al.\[290\] theoretically compared the operation of a potential magnetocaloric refrigerator equipped with micro-Peltier thermal switches with thermal resistances that were varied by a magnetic field with parallel-plate active magnetic regenerators. The former was found to be superior and with an optimal operation frequency above 20 Hz. Another theoretical study of Peltier thermal switches was performed by Egolf et al.\[291\] who investigated the application of Ni-nanowire-based Peltier thermal switches to a magnetocaloric refrigerator and compared the results with the operation of a magnetic refrigerator. They found that the specific cooling power density of a device with thermal switches can be as much as five times that of a comparable AMR-based device. In another theoretical study, Monfared\[292\] numerically simulated a cascade arrangement of Peltier modules with integrated magnetocaloric material. They reported a rather small cooling power of 156 W kg$^{-1}$ of magnetocaloric material at an operating frequency of 10 Hz. Another comprehensive theoretical study on the use of micro-Peltier modules as thermal switches was performed by de Vries and van der Meer.\[293\] The authors reported a less optimistic outlook of the technology. Nevertheless, the argument was made that a heat pump based on only Peltier modules could perform better than one that combined micro-Peltier modules with a magnetocaloric material. The first experimental evaluation of this proposition was performed in 2017 by Puga et al.\[294\] who utilized a ferrofluidic thermal switch. The motion of the ferrofluid was driven in one direction by the magnetic field and in the other by gravity. Good performance was achieved at frequencies of up to 30 Hz. Bartholomé et al.\[295\] investigated the application of the heat-pipe principle to a magnetocaloric refrigerator. They reported significant advantages compared with active magnetic regeneration, including no requirement for pumps, improved heat transfer of the phase change fluids utilized, high frequencies >10 Hz, and significantly reduced device cost. In a subsequent study, the authors proposed a new, universal analytical model\[296\] for simulations of the cascade operation of caloric cooling devices that use thermal switches or thermal diodes. The model was validated by comparing its results with those of other numerical models and with experimental results. In 2017, Lei et al.\[297\] conducted a numerical and experimental study to evaluate the mechanism of magnetohydrodynamic (MHD) convection for application to magnetic refrigeration. Another type of magnetocaloric refrigeration system that utilizes thermal switches was numerically simulated and experimentally validated by Wu et al.\[298\] The system consisted of two rotating discs with compartments of the magnetocaloric material, separated by spaces into which other copper-based discs were inserted. The latter discs facilitated periodic heat transfer between the different parts of the two rotating discs and therefore acted as thermal switches. The results revealed a 50.9 K maximum temperature span between the heat source and heat sink, with a specific cooling power of 105.8 W kg$^{-1}$ of magnetocaloric material. The magnetic field change was considered to be 1.5 T. In a subsequent study, the authors improved the numerical model by modifying the discs.\[299\]

The above discussion reveals significant differences between the results obtained by different researchers. It should be emphasized that the transient heat transfer problem with multiple variables is difficult to address by tuning the variables over larger value ranges. This is especially so when the full thermal properties, anisotropic properties, phase change, or multiphysical problems are involved. However, without accurate models and comprehensive simulations covering the broad spectrum of the different parameters, it is possible to overlook the efficient operation of a certain thermal control element. However, by determining the desired requirements for the operating conditions, it would not be very challenging to filter out unacceptable solutions and identify the thermal control elements with high thermal masses for fast-response solutions. In 2015, Kitanovski et al.\[300\] presented an up-to-date, comprehensive overview of the potential applications of thermal switches and thermal diodes in magnetocaloric energy conversion (Figure 8). The work covered a large number of interdisciplinary domains that contribute to thermal control in magnetocalorics. However, the most comprehensive review of research on thermal control elements in caloric technologies can be found in the following reference.\[301\] The work includes the targeted features of thermal control elements used for caloric energy conversion.
2.6. Magnetic Field Sources

In addition to the magnetocaloric material, the magnetic field source is another critical part of a magnetic refrigerator or heat pump. Magnetic field sources are of four main types, namely, permanent magnet assemblies, superconducting magnets, electromagnets, and hybrids (i.e., electro-permanent magnets). All permanent magnet assemblies used in magnetic refrigerators or heat pumps include a driving system or motor and a gear drive. This are used to provide a variable magnetic field through the linear movement or rotation of the magnetocaloric material relative to the static magnetic field source. In another case, the variable magnetic field is provided by the linear movement or rotation of the permanent magnet assembly. In the case of a superconducting magnets or electromagnets, they mostly consist of a variable magnetic field with linear movement of the magnetocaloric material. Whereas the magnetic field source is a crucial part of a magnetocaloric device, it is also the heaviest and most expensive part. The first review on magnetic field sources for magnetocaloric refrigeration and heat pumping was presented by Bjørk et al. in 2010. This was followed in 2015 by an up-to-date and comprehensive review.

2.6.1. Superconducting Magnets

Earlier works on room-temperature magnetic refrigeration mostly utilized superconducting magnets, such as in the first prototype device developed by Brown. A review of a few subsequent prototype devices can be found in the following two references. All these devices generally operated with a rather low frequency and produced a very strong magnetic field, which contributed to the generation of a wide temperature span between the heat source and heat sink. Superconducting magnets are a strong subject in low-temperature physics, and a brief mention has already been made of them in this manuscript. However, they are too costly for small-scale magnetocaloric refrigeration or heat pumping near room temperature. Actually, there has been no experimental study on the applicability of superconducting magnets to large-scale magnetocaloric refrigerators or heat pumps at room temperature.

2.6.2. Permanent-Magnet Assemblies

Since 2015, most of the relevant research works have focused on the optimization and design of rotary permanent magnet assemblies using a Halbach array. Such permanent magnets consist of only the permanent magnet material or a combination of the material and a soft ferromagnetic material. In 2015, Trevizoli et al. reported the design and experimental validation of a nested Halbach assembly. A numerical simulation of a multi-polar Halbach cylindrical magnet was also conducted by You et al. in 2016. Numerical simulations of several design configurations of a rotary permanent magnet assembly were performed by Lorenz and Kevlishvili in 2017. In 2017, Fortkamp et al. presented a parametric analysis of the performance of nested permanent-magnet Halbach cylinders. This interesting study also included analytical solutions of Maxwell's equations, which were used to investigate the performance of the magnetic circuit. Another numerical study was performed by Mira et al. who evaluated the magnetization of the magnetic fields of different types of active magnetic regenerators. The study considered different magnetic sources including an electromagnet, a permanent magnet in a soft ferromagnetic toroidal yoke, and 2D and 3D Halbach cylinders. Because the temperature and the arrangement of the magnetocaloric matrices significantly affect the magnetic field, these factors should be carefully taken into consideration in the design of permanent magnetic field sources. A classic octagonal Halbach permanent magnet assembly was numerically evaluated in 2018 by Celik and Kural. Recent years have also witnessed several studies on the optimization of the topology of permanent magnet assemblies. The most recent studies were conducted in 2018 by Lee et al. and Teyber et al.
2.6.3. Electromagnets

Electromagnets have been used specifically for the purpose of testing magnetocaloric regenerators. They were only recently applied to magnetic refrigeration and heat pumping.[315] The on–off operation of a conventional electromagnet is rather slow, implying a low operation frequency. Operations at higher frequencies would require the use of a permanently activated electromagnet with movement of the magnetocaloric regenerator. Gao et al.[316] (very high magnetic field of 2.18 T), Bahl et al.[317] (1.4 T), and Shassere et al.[318] (0.75 T) employed electromagnets with linear movement of the magnetocaloric regenerator. In 2009, Coelho et al.[319] reported the use of a 2.3 T electromagnet that was permanently switched on, and periodic magnetization/demagnetization was achieved by moving a rotating wheel containing magnetocaloric materials through the gap of the magnet. The problems associated with low-efficiency Joule heating and very low-frequency operation were recently largely solved[315] through the use of a highly energy-efficient electromagnetic field source—with the magnetic energy regeneration. The ability to operate at very high frequencies (>15 Hz) was achieved by a specially designed electronic circuit with a capacitor.

2.6.4. Magnets and Their Resources

Researchers are investigating problems associated with rare-earth-based magnetic field sources. Gauß et al.[316] evaluated Nd and Nd-Fe-B as candidate permanent-magnet materials for magnetic refrigeration. They emphasized that rare-earth permanent magnets could constitute a significant bottleneck toward the commercialization of magnetocaloric refrigeration and heat pumping. In 2017, De Almeida et al.[320] identified a similar problem of rare-earth permanent-magnet materials in relation to their use in motors, namely, price instability/uncertainty due to the concentrated production of rare earth metals and the environmental impact of their mining and refining. To address these challenges, researchers are seeking for alternative permanent-magnet materials with significantly lower heavy rare earth contents.[121] Unless good alternative and sustainable materials are found in the future, the recycling of magnets will become a crucial issue in the future.[322]

2.6.5. Figure of Merit for Permanent Magnet Assemblies

One way of reducing the content of rare earth metals in a permanent magnet assembly is by optimizing the design. An important need in this regard is a figure of merit for the magnetic performance of a permanent magnet assembly. Such a figure of merit was introduced in 2008 by Björk et al.[323]

2.6.6. On a General Figure of Merit for Magnetic Field Sources

There are two very important figures of merit that can be adopted for the future design and comparison of magnetic field sources used for magnetic refrigeration and heat pumping. One of them is related to the energy efficiency of the magnetic field source, and can be defined as the ratio of the ideal net magnetic work (or power, considering the cycling) to the ideal net magnetic work plus all the different losses that occur in the magnet system during its operation (i.e., losses due to or in motor, gear drive, bearings, electric coil Joule heating, eddy currents, control electronic circuits, power supply variation, etc.). To the best knowledge of the author, the use of energy efficiency as a figure of merit for comparing different magnetic field sources has not been extensively evaluated using different magnetic field sources and different configurations. However, there has been a publication of an attempt to compare a static electromagnetic field source and a rotary permanent magnet assembly.[315] The second figure of merit is related to the economics of the device. Considering the variable cost of materials, it makes sense to avoid direct costing. Rather, a breakdown can be made in terms of the required masses of specific materials (e.g., rare earth Nd-Fe-B and iron) per magnetized volume of the empty gap, or per ideal net magnetic work. Other related factors include environmental impact and resource availability.

2.7. Hydraulic Circuits

There is a huge fluid dynamics challenge in active magnetic regenerators and the important research subject on hydraulic circuits in magnetocaloric refrigerators and heat pumps. Researchers tend to search for solutions that reduce the dead volumes or potential mass flow imbalance through the entire hydraulic circuit. Moreover, the high frequency of the operation involves rapid oscillation of the fluid flow through the porous matrix of the magnetocaloric regenerator, resulting in large pressure losses. The challenge is also to control the hydraulic circuit during the operation of the device.

Generally, and with regard to the state of the art, there are two types of fluid propulsion systems, namely, bidirectional and unidirectional propulsion systems. The application of these systems depends on the way that the variable magnetic field is applied to the active magnetic regenerator. In the case of a static active magnetic regenerator, the magnetization is generated through the motion of the magnetic field source, or by an on–off operation of the electromagnetic field source. These are the kinds of systems generally used nowadays. The fluid propulsion in this particular case can be provided by the displacement of a piston, which may be driven hydraulically, pneumatically, electromagnetically, or mechanically. Other means of bidirectional fluid propulsion include gear pumps, membrane pumps, and peristaltic pumps. A tandem of unidirectional pumps can also be used to produce the oscillatory flow. However, experience with prototyping reveals that such a system can only provide good control of the pressure inside the hydraulic circuit at low operation frequencies. Bidirectional fluid propulsion, in the hydraulic circuit of magnetic refrigeration or heat pumping, is implemented with the use of check valves or cam valves.[322,124] A static active magnetic regenerator also enables the use of a unidirectional pump. However, such a system requires a rotary valve[265,123] or valve assembly such as of solenoid valves[326] for continuous operation of the pump while maintaining the oscillation of the fluid flow. Cam valves[327] may also be used.
2.8. Prototypes and Devices

Magnetocaloric refrigerator and heat pump prototypes can be divided into three main types, namely, linear, rotary, and static devices, with respect to their motion during the magnetization/demagnetization of the magnetocaloric material. In linear devices, the magnetization/demagnetization is accomplished by the movement of the magnetic field source over the static magnetocaloric regenerator. In rotary devices, the magnetization/demagnetization is accomplished by the rotation of the magnetocaloric material into the magnetic field produced by the static magnetic field source. In another version of this type of devices, the process involves the rotation of the magnetic field source over the static magnetocaloric material. This configuration is one of the most utilized in recent prototype devices. An earlier method involves the rotation of the magnetocaloric material through the magnetic field produced by the static magnetic field source. In the case of static devices, with the exception of the working fluid, the other parts including the magnetic field source and magnetocaloric material are at rest. In most of the different types of devices, the magnetocaloric material constitutes the active magnetic regenerator.

More than 80 different concepts or prototypes of magnetocaloric refrigerators and heat pumps have been put forward till date. The most comprehensive review of these prototype devices up to 2015 was presented by Kitanovski et al.[31,35] However, the domain is witnessing rapid developments and a single year may bring important improvements. The latest reviews of magnetocaloric devices were presented by Trevizoli et al.,[128] Zimm et al.,[229] Kitanovski et al.,[110] and Greco et al.[131] A lifetime cost analysis and life-cycle assessment of magnetic refrigeration were also undertaken by Björk et al.[332] and Luglietti et al.[333]

The most developed prototypes so far were presented by the French company Cooltech Applications, which has applied magnetic refrigeration in real devices. The company announced the end of their activities at the IIR Thermag VIII Conference in Darmstadt in 2018. However, most recently, the team from Cooltech Applications established a new company Ubiblue in France, as announced at Delft Days on Magnetocalorics DDMC 2019 in Delft, Netherlands. The last 5 years has particularly witnessed a number of relevant studies and the development of prototype devices. Most of the works concerned the application of permanent-magnet assemblies based on a linear or rotary principle. To avoid duplicating previous effort, the review here will be limited to works over the last 5 years.

2.8.1. Linear Magnetocaloric Refrigeration Prototypes and Experimental Devices

Jawad Mahdy et al.[334] reported the development of a linear magnetocaloric testing device consisting of a conventional Halbach permanent magnet assembly. In the same year, Lee[335] developed and tested a twin-regenerator-bed linear magnetocaloric device. The bed contained 0.25 mm Gd spheres and was linearly driven by a pneumatic cylinder and an actuator. Another device with linear movement of the permanent magnet assembly and a maximum magnetic field of 0.8 T was developed by Kolano et al.[336] The authors used two active magnetic regenerators consisting of parallel Gd plates. Lei et al.[207] described a reciprocating testing device for the experimental evaluation of active magnetic regenerators. The reciprocating movement of two cylinders in the device generated the oscillatory flow through the porous regenerator. No magnetic field source was utilized. The device importantly enabled investigation of the effectiveness of active magnetic regenerators. A linear magnetocaloric testing device with the movement of the active magnetic regenerator through a Halbach magnetic field source was recently reported by Czernuszewicz et al.[337] Kondo et al.[228] conducted an experimental study on different types of Gd-based magnetocaloric regenerators. The highest specific cooling power obtained in the study was 298 W kg\(^{-1}\) at an operating frequency of 10 Hz. Ekren et al.[338] developed an experimental magnetic refrigerator consisting of a linear motion system and a pair of 0.7 T permanent magnet assemblies. The Gd bed of the system was set in motion by a linear mechanism and brushless DC motor.

2.8.2. Rotary Magnetocaloric Refrigeration Prototypes and Experimental Devices

Aprea et al. in 2015[339] and 2016[340] reported on experiments performed on a rotary magnetic refrigerator consisting of a Halbach array with a high average magnetic field of 1.10 T. The refrigerator consisted of eight radially arranged regenerators filled with Gd spheres with a total mass of 1.20 kg. The drive system consisted of a brushless DC motor that rotated the magnets at variable speeds of 0.1–1 Hz. The device achieved a maximum cooling power of 190 W. For a temperature span of 6 K, the device produced 100 W with a COP of 0.6. In 2017, the same group implemented an artificial neural network[341] for optimizing the performance of a rotary magnetic refrigerator. Albertini et al.[342] conducted a preliminary study of a prototype rotary magnetic refrigerator consisting of four static active magnetic regenerators and a rotor with two permanent magnet assemblies. In 2018, Johra et al.[343] reported the numerical evaluation of a magnetic heat pump that could be integrated into a single hydronic loop including a ground-source heat exchanger and a radiant under-floor heating system. The device was designed for a maximum heating power of 2600 W and consisted of 13 regenerators arranged in a trapezoidal form and with beds packed with 0.45 mm spheres. These were placed between the stator and a two-pole permanent magnet assembly positioned on the rotor. The fluid flow was thus provided in the radial direction through the regenerator beds. A test and numerical evaluation of a rotary magnetic heat pump were also presented by Johra et al.[344] In 2018, Chaudron[345] reported on the largest rotary magnetic refrigerator device ever created, designed to provide 15 kW of cooling power with a 20 K temperature difference between the heat source and heat sink. The device had 32 compartments for active magnetic regenerators. However, its preliminary testing was conducted with only two regenerators that utilized five Gd and Gd alloy materials with different Curie temperatures. The rotating four-pole magnet assembly was set in motion by an external motor through a shaft. The working fluid flow was driven by a circulation pump.
and the synchronization of the cycle phases was executed using custom mechanical valves. The authors reported 60% second-law efficiency for the preliminary testing. In 2016, Lozano et al.\cite{325} designed a rotary magnetic refrigerator. The magnetization/demagnetization was provided by the rotor (permanent magnet assembly)–stator (soft iron) configuration, with a maximum magnetic flux density of approximately 1 T. The prototype consisted of eight pairs of stationary regenerator beds filled with approximately 1.7 kg of Gd spheres (diameter 425–600 µm) and placed in the magnetic gap. Two rotary valves were used to synchronize the hydraulic and magnetic cycles. The maximum no-load temperature span was reported to be 12 K at 1.5 Hz, while the maximum zero-temperature span cooling power was 150 W at 0.8 Hz. At a cooling power of 80.4 W and operation frequency of 0.8 Hz, the device provided a temperature span of 7.1 K with a COP of 0.54 and second-law efficiency of 1.16%. Another performance evaluation was performed by Capovilla et al.\cite{346} who reported a maximum second-law efficiency of 3.70% for a temperature span of 6 K. For a system with ideal valves, they reported a second-law efficiency of 5.75% for an operating frequency of 0.4 Hz and system temperature span of 4 K. The authors noted the occurrence of a large pressure loss at the rotary valves and the magnetic circuit rotor, corresponding on average to approximately 91% of the power consumption of the transmission system. They also explained the significant losses that occurred in the valves and bearings, and the power required to rotate the magnet during acceleration and deceleration of the rotor. The study was followed up with further experiments\cite{231} using different porous-matrix geometries of the active magnetic regenerators. The authors reported a maximum second-law efficiency of about 7% with a 12 K temperature span for regenerators consisting of pin arrays. Benedict et al.\cite{347} reported on a rotary magnetic refrigerator consisting of two nested Halbach magnet assemblies, which provided high and low magnetic fields of 1.5 and <0.1 T, respectively. Each of the two regenerators contained irregular Gd particles with sieve fractions of 1.0 and 1.4 mm, respectively, and of length 160 mm. The maximum no-load temperature span was reported to be 21 K and the maximum cooling power of 26 W was achieved with a temperature span of 1 K. Benedict et al.\cite{348} experimentally investigated the effects of the magnet and regenerator design on the refrigeration performance. A very interesting experimental study was also conducted by Gao et al. in 2016,\cite{349} in which a high-pressure hybrid refrigerator was combined with an active magnetic regenerator operated on the Stirling refrigeration cycle. The helium-gas-filled alfa-type Stirling refrigerator had a regenerator composed of Gd plates, which simultaneously served as an active magnetic regenerator in a magnetic field that varied between 0 and 1.4 T. The system produced cooling powers of 40.3 and 56.4 W over temperature spans of 15 and 12 K, respectively. In the latter case, the cooling power improved the operation of the Stirling cycle by 28.5%. Another rotary magnetic refrigerator was recently developed by Krautz et al.\cite{350} as an air conditioning system, capable of generating magnetic flux densities of >1.4 T. It consisted of an inner rotor with eight iron teeth, a stator with four-pole permanent magnets, and an outer iron yoke. The magnetocaloric material chambers were placed in the stator. The epoxy-bonded plates with 55 vol% LaFe$_{11.5}$Si$_{1.2}$Mn$_{0.3}$H$_{1.8}$ were produced by tape casting and had a total weight of 300 g. Huang et al.\cite{351} recently reported another rotary magnetic refrigeration prototype, with a rotary magnetic field source that generated an average magnetic field of 0.875 T. The device utilized seven asymmetrically arranged packed-bed Gd regenerators with a total mass of 1.18 kg, and a real-time-controlled programmable solenoid valve system was used to produce the synchronized fluid flow. The authors reported a maximum zero-temperature-span cooling power of 162.4 W, and a zero-power temperature span of 11.6 K.

### 2.8.3. Numerical Investigations of Magnetocaloric Refrigerators

Several numerical studies have considered magnetic refrigerators and their performance. Through numerical simulations and experimental validation, Monfared\cite{352} comprehensively investigated the performance of regenerators for a rotary magnetic refrigerator. The rotating magnet assembly consisted of a permanent magnet assembly as the rotor, and a soft ferromagnetic cylinder as the stator. The prototype device was composed of 12 regenerator beds inserted coaxially into the cylinder between the rotor and the stator. Niknia et al.\cite{353} used a comprehensive parametric numerical analysis to investigate the impact of losses on the performance of a magnetic refrigerator consisting of two concentric nested Halbach arrays with inner cylindrical regenerators. A displacer was used to pump the working fluid through the system, and check valves were used to control the flow direction. They observed a very high second-law efficiency of 75% at a very low operation frequency of 0.5 Hz. An increase of the operation frequency to 3 Hz decreased the second-law efficiency to about 40%. Qian et al.\cite{354} used the Simulink software to model a room-temperature magnetocaloric cooling system, in one of the first examples of the approach. They considered a linear system consisting of a tandem of two active magnetic regenerators and a permanent magnet assembly. A very interesting study was also performed by Silva et al.\cite{355} who performed a numerical simulation of a simple magnetocaloric material exposed to a sweeping magnetic field without fluid flow. The authors reported a temperature span of >20% of the maximum adiabatic temperature span of Gd, which was the material used for the modeling. In another recent study, the same author\cite{356} evaluated the application of the heatrapy Python framework to simulating caloric effects and thermal devices. In this work, two simple models of a fully solid-state magnetocaloric system and a hydraulic active magnetic regenerative system were implemented and the results were verified. Both model simulations were found to considerably reduce the computational costs.

Below, we briefly explain the operation of different types of magnetocaloric refrigeration and heat pumping devices that have been designed through time.

**Linear Magnetocaloric Refrigerators and Heat Pumps with Permanent Magnet Assemblies:** Linear types of devices mostly serve as experimental versions for testing active magnetic regenerators. In contrast, superconducting magnets were mostly applied in the past, which is not the case anymore, except for experiments involving low-temperature physics. Moreover, recently, researchers have applied rotary devices for investigating the
performances of active magnetic regenerators. This is because of the potentially high frequency of operation, including the faster variation of the high/low magnetic field in the magnetocaloric sample. A single linear system provides discontinuous cooling. To ensure continuous operation, a tandem of two magnetic field sources and two magnetocaloric materials can be used. Most linear devices consist of permanent-magnet assemblies (Figure 9). Linear operation is also used for conventional electromagnetic field sources, mostly with the movement of the magnetocaloric regenerator.

Rotary Magnetocaloric Refrigerators and Heat Pumps: Most prototype devices belong to this group of magnetocaloric refrigerators and heat pumps, and in most recent devices, the magnetocaloric material is static. The examples in Figure 10 show the most commonly applied operational principles. In the case of a nested Halbach structure (see, e.g., study by Trevizoli et al.[306]), the internal or the external ring of the permanent-magnet structure rotates while the other ring remains at rest, thus periodically magnetizing/demagnetizing the static magnetocaloric regenerator. The operational principal of the Halbach-iron assembly (see, e.g., study by Bjørk et al.[312]) is similar to that of the nested Halbach assembly. However, the rotary Halbach-iron assembly consists of a reduced mass of permanent-magnet material, thus representing a more optimized example of the magnetic field source, compared to the nested Halbach assembly. Moreover, it simultaneously provides demagnetized and magnetized regions, which allows continuous device operation. This magnetization/demagnetization occurs either by rotation of the internal ring, consisting of active magnetic regenerators. Another very efficient method involves operating the magnetocaloric refrigerator with the two- or a multipole assembly of the rotor-stator (see, e.g., study by Lozano et al.[325]). In this particular case, for example, the stator is fabricated from soft iron and serves as a guide for the magnetic flux, while preventing leakage of the flux out of the assembly. The rotor consists of a rotating permanent-magnet assembly which provides magnetization/demagnetization over the magnetocaloric regenerators. Another more special case is presented in the bottom right panel of Figure 10. In this particular case, the motor drive and the magnetizer of the magnetocaloric materials represent a single assembly. The electric coils in combination with the permanent magnets engage in an attractive or repulsive force, which creates a torque and simultaneously provides controlled rotation, similar to the case of the permanent-magnet stepper motors.[35]

The above examples are not the only options for a rotary magnetic refrigerator or a heat pump. These devices can be distinguished using the direction of fluid flow through the magnetocaloric material. Apart from the prototypes based on nested Halbach configurations, most active magnetic regenerators of rotary magnetocaloric devices are coaxial cylinders, consisting of a single magnetocaloric material or magnetocaloric material, layered in the direction of the temperature gradient. Thus, one can distinguish between the axial, radial, and azimuth flow devices. The fluid flow of axial flow devices is in the direction of the main axis of the active magnetic regenerator (examples given in Figure 11). In radial flow devices, the working
fluid flows in the radial direction through the active magnetic regenerators. The second magnetic refrigerator prototype device based on permanent magnets, which has also been extensively researched and has certainly contributed to the expansion of the research activities in this domain, was developed in 2001.\textsuperscript{[357]} In this prototype, a rotating ring consisting of magnetocaloric materials rotating through the static permanent-magnet assembly is applied. The working fluid flow is distributed with the help of the rotary valve system. The working fluid also flows through the beds of the active magnetic regenerators in the azimuth direction.

**Static Magnetocaloric Refrigerators and Heat Pumps:** There exists no practical solution for the application of only permanent-magnet assemblies that can ensure static switching of the high- and low-magnetic-field regions. This solution, however, can be applied in the case when these assemblies are combined with electric coils. The first idea of a fully static magnetocaloric refrigerator or a heat pump can be traced back to the patent of Chilowsky in 1952.\textsuperscript{[142]} By solving the challenge of high and low fields, a fully static magnetocaloric refrigerator can be designed using an electro-permanent-magnet assembly, for example, by introducing thermomagnetic power generation.\textsuperscript{[358]} Experimental magnetocaloric prototype devices with a conventional electromagnetic field source exhibit a rather slow magnetization/demagnetization process. The long magnetization and demagnetization processes affect the low frequency of the operation. Because of these long-lasting processes and the unavoidable Joule heating in conventional electric coils, active cooling is necessary. Recently, the problem of slow magnetization/demagnetization, related to conventional electromagnets, has been solved. Moreover, the same solution (Figure 12) ensures regeneration of magnetic energy, which makes electromagnets especially interesting for applications at frequencies of operation higher 5 Hz.\textsuperscript{[315]} Such a fully static application in the form of a magnetic wine cooler was recently presented by Tomc et al.\textsuperscript{[359]}

![Figure 10. Examples of the rotary operation principle of a magnetocaloric refrigerator or a heat pump (top-left) Nested Halbach structure; (top-right) Halbach-iron assembly; (bottom-left) a two-pole rotor-stator configuration; (bottom-right) multi-pole hybrid electro-permanent-magnet assembly. Adapted with permission. Copyright 2015, Springer.](image1)

![Figure 11. Examples of the rotary principle of operation of magnetocaloric refrigerator or heat pump: (left) radial flow of the fluid through the coaxial cylinder consisted of active magnetic regenerators; (right) azimuth flow of the fluid through the coaxial cylinder consisted of active magnetic regenerators.](image2)
3. Heat-to-Power Conversion with Magnetocaloric Materials

The thermomagnetic conversion of heat into useful work has been revisited in the past 20 years, and extensive research has been conducted in the past decade. In general and similar to magnetocaloric refrigeration and heat pumping, magnetocaloric heat-to-power conversion can be performed utilizing the linear motion of magnetocaloric materials, its rotation, and a fully static device configuration. These principles are thoroughly described and supported by examples in the following subchapters.

Different magnetocaloric power-generation devices were reviewed recently by Kishore and Priya [97] and Ferreira [360]. Moreover, Gao et al. [83] and Vopson [361] reviewed power generation with different ferroic materials. Numerous studies in the past decade have theoretically evaluated different ferromagnetic materials in energy harvesting. A comprehensive feasibility study for the Swiss Federal Office of Energy on magnetocaloric power generation was performed in 2008 by Kitanovski et al. [362] and in 2009, by Egolf et al. [363]. In 2011, Hsu et al. [364] evaluated the potential efficiency of thermomagnetic power generation by different ferromagnetic materials. The study focused on polycrystalline and single-domain Gd exposed to a magnetic field change of 0.3 T and a temperature change of 5 K between the heat source and the heat sink. The study revealed considerably low energy efficiency. They reported the second-law efficiency being 30.4% for single-domain Gd, and a nearly three-times-smaller second-law efficiency with polycrystalline Gd. Song et al. [365] reviewed and thermodynamically studied the application of Heusler alloys for power generation. Post et al. [366] theoretically investigated the energy-conversion efficiency of Heusler alloys and revealed a 15.9% second-law efficiency for an applied magnetic field of 0.3 T, and 63.8% for an applied magnetic field of 1.5 T. Ferreira et al. [367] performed a comprehensive numerical computational fluid dynamics (CFD) analysis for different channel geometries in regenerators suitable for a thermomagnetic engine. Almanza et al. [368] compared the thermomagnetic and thermoelectric power generation and revealed that thermomagnetic power generation can be more efficient and has a slightly higher power density than thermoelectric power generation for a temperature difference of lower than 10 K between the heat source and the heat sink. The authors concluded that low-grade-heat thermal energy harvesting could be considered for thermomagnetic generation.

The influence of first- and second-order ferromagnetic materials on the energy efficiency of magnetocaloric power generation was investigated by Almanza et al. [369]. They calculated the theoretical second-law efficiency for both types of materials and observed that the highest second-law efficiency was 45% [370]. In 2017, Bessa et al. [371] reported a numerical study of first- and second-order materials with respect to the performance of thermomagnetic motors. Their results show that first-order materials with a large thermal hysteresis can perform more specific work compared to first-order materials with small hysteresis or second-order materials. They further explained that in materials with a large hysteresis, a large amount of heat accumulates in the material before the ferromagnetic-paramagnetic transition and that the part of the former is converted into work. Consequently, the high amount of stored heat leads to higher work...
production. Furthermore, Kishore and Priya[172] provided a list of 61 alloys with the potential to be applied in magnetocaloric power generation and outlined the 10 most promising alloys.

Although magnetocaloric power generation can be based on several different operating principles, all the existing prototype devices in general operate with a very small power density or low energy efficiency. Few reasons for this can be found by using advanced knowledge from magnetocaloric refrigeration and heat pumping. An important reason is that researchers apply rather large temperature gradients over a single magnetocaloric material. Clearly, the largest changes in magnetization occur in the vicinity of Curie temperature. In addition, by stretching the operating temperature interval, the thermomagnetic efficiency will certainly decrease for single magnetocaloric materials. Therefore, for the large temperature differences between the heat source and heat sink, a layered magnetocaloric material should be used. However, this is not so evident is that large magnetic fields contribute first to the possibility of the operation for larger temperature spans, contribute to the higher power density, and affect the second-law efficiency. Furthermore, the small power density along with the efficiency is related, similar to magnetic refrigeration at a low frequency of operation and a non-optimized heat transfer. Moreover, one can see that most researchers do not apply heat regeneration, which was actually identified to be very important for magnetocaloric power generation in the 1960s. In spite of this critical view of research activities, it is important to emphasize that the devices presented in the subsequent chapter are very much pioneering experimental work. Namely, most of the earlier studies, despite their descriptions of certain designs, were only theoretical.

3.1. Static Magnetocaloric Power Generators

Most work done in this particular subdomain relates to the earlier work of Brillouin and Iskenderian[141]. In 2011, Srivastava et al.[173] reported the development of a static generator, consisting of a cylindrically shaped specimen of Ni$_5$Co$_5$Mn$_{40}$Sn$_{10}$. This was fixed near the pole of a cylindrical magnet, placed below the specimen, which was surrounded by a copper coil. The heat source was provided by a heat gun. The authors concluded that the applied low hysteresis alloy and the application give the most promising results for the potential future applications of low-grade thermal energy conversion. Christiaanse and Brück[174] performed numerical and experimental research on a device consisting of two active (Mn,Fe)$_2$(P,As) magnetic regenerators, where each of them consisted of disks of (Mn,Fe)$_2$(P,As) with four different Curie temperatures. The Nd-Fe-B permanent magnet acted as the magnetic field source. A theoretical and experimental study on a static thermomagnetic power generator was performed by Lallart et al.[175] In the first configuration, they experimentally tested the assembly, consisting of a copper wire coil around back iron, which served as the magnetic flux guide between the two Nd-Fe-B magnets and the ferromagnetic alloy, consisting of 30% nickel and 70% iron. Later, they theoretically investigated the possibility of replacing the back iron with a ferromagnetic alloy, which led to a higher power density compared to the basic device. The authors did not comment on the energy efficiency of these devices. However, they emphasized that the energy-conversion efficiency is not only related to the absolute variation of the permeability of the materials but is also related to the mean permeability value through the inductance. Furthermore, they showed that from the material point of view, using materials showing a sharper decrease of permeability but with a high mean permeability value, such as Gd, would not significantly increase the total power density. In 2018, an investigation of the configuration of a thermomagnetic generator was performed by Zhang et al.[176]

The authors considered two blocks of Gd, located next to Nd-Fe-B magnet and covered by two layers of iron at both ends. Both the magnet and two regenerators were believed to be attached to soft iron at both ends. Based on periodic heating and cooling of the magnetocaloric material, the magnetic field inside the copper coil changed in time, thus generating an alternating current. Based on the results of this study, the authors report that the second-law efficiency was 54%. The most recent work on a fully static magnetocaloric power generator (Figure 13) was reported by Waske et al.[158] The authors first studied several different potential configurations of permanent magnets, magnetocaloric materials (La-Fe-Co-Si-based plate magnetocaloric regenerators), steel yokes, and electrical coils. Based on the numerical results, they chose the best configuration, which was further experimentally validated. The authors reported that the very low second-law efficiency was a consequence of the non-optimized device configuration and its parts.

3.2. Rotary Magnetocaloric Power Generators

A thermomagnetic wheel is a continuously rotating device and is the main component of a rotary magnetocaloric power generator (Figure 14). The wheel consists of a ferromagnetic material and a magnetic field source. The latter can be a permanent-magnet assembly or an electrical coil. An important part of such an engine is the heat sink and the heat source heat exchangers. These are required to establish a temperature gradient, which, in contrast, affects the temperature-dependent magnetization of the wheel. Wheel rotation is, therefore, a consequence of the net-magnetic force that is a result of the temperature-dependent magnetization of the wheel, caused by the heat source and the heat sink, in combination with the externally applied magnetic field.
In 1998, Andreevskiĭ et al.\cite{378} presented a short description on the thermodynamic characteristics of thermomagnetic engines, and referred to them as a thermomagnetic wheel. They provided expressions for the work and efficiency of a thermomagnetic engine as a function of thermal and magnetic properties of the working material. In 2001, Karle\cite{379} theoretically studied the dynamic behavior of a thermomagnetic wheel heated by solar radiation.

Two reports on a rotary thermomagnetic engine were published in 2004 by Takahashi et al.\cite{380} The authors reported on the theoretical analyses, design, and experimental validation of a single and a multiple disc, rotating through three zones of the magnetic field provided by permanent-magnet assemblies. The material used in the experiment and analyzed was the magnetic shunt alloy Fe$_{54}$Ni$_{36}$Cr$_{10}$. Before and after each magnet assembly, a heat source and heat sink were provided. An interesting experimental study, albeit with magnets, was performed in 2006 by Palmy.\cite{381} The device consisted of a levitating, thin, cylindrical permanent magnet between two poles of static permanent magnets. The levitating magnet was then heated by an external laser source, which caused it to rotate. Trapanese et al.\cite{382} designed, simulated, and experimentally validated a rotary magnetocaloric power generator consisting of a rotor holding Gd powder. Unfortunately, the authors did not report the performance of the device. The utilization of the industrial waste heat by magnetocaloric rotors was theoretically studied in 2012 by Vuarnoz et al.\cite{383} In the two publications of Alves et al.\cite{384,385} the authors reported a simulation and comparison of the performance of solar-driven thermomagnetic wheels consisting of Gd and MnAs. A model for the magnetic circuit was also developed. The authors commented that the Gd and MnAs as magnetocaloric materials offer about one-order-of-magnitude more power than 30% NiFe alloy. The authors further showed the design scheme for the experimental bench engine prototype. Gabrielyan et al.\cite{386} performed a theoretical study on the use of heat from power plants for magnetocaloric power generation.

In 2016, Achkar et al.\cite{387} theoretically evaluated magnetocaloric power generation by utilizing the waste heat from the rotary movement of a magnetocaloric material. The latest research on thermomagnetic wheels reported on the design, analyses, and experimental validation of the prototype device by Kishore et al.\cite{372} The authors designed, analyzed, and tested the thermomagnetic wheel structure consisting of up to six rotors of Gd magnetocaloric material. The device looked similar to the one presented in the left panel of Figure 14. The device could convert energy with very low temperature differences between the heat source and the heat sink by only 2 K.

### 3.3. Linear Magnetocaloric Power Generators

The basic operation of a linear device is shown in Figure 15. When the rod has a uniform temperature, it remains in equilibrium in the magnetic field. When a temperature gradient is established at both halves or ends bordering the high and low magnetic field regions, there will be a force acting on the rod in the direction of the temperature gradient (cold-to-hot). When a spring and coil generator is added to the rod, electric power will be generated and finite length of the rod will return back to its starting position, leading to a capability to perform a continuous operation with n-cycles (Figure 15, middle). If one uses the crank shaft, the linear motion will be translated into rotary

---

**Figure 14.** Schematic examples of the thermomagnetic wheel: (left) the device consisted of a heat reservoir as the heat source and the ambient as the heat sink; (middle) gases or air as the working fluids; (right) device uses liquid as the working fluid.

**Figure 15.** The basics of linear magnetocaloric power generators: (left) a simple rod exposed to a temperature gradient before and after the magnetic field; (middle) a rod attached to the spring and electric coil; (right) from linear to rotary motion.
motion (Figure 15, right). These three examples give the basis for other linear thermomagnetic prototype devices.

In 2017, Viola et al.\cite{388} reported a prototype linear thermomagnetic motor, which was designed and theoretically investigated a few years earlier.\cite{389} The generator was composed of 12 Nd-Fe-B permanent magnets and two plates of Gd\textsubscript{4.7}Nd\textsubscript{0.3}Si with internal channels for the flow of heat-transfer fluid. Hydraulic valves and other sensors were used to control the working operations, while a slider-crank mechanism transformed the permanent magnet’s oscillatory motion into revolving motion. A similar example is shown in the right panel of Figure 15.

In 2007, a small prototype of a linear magnetocaloric engine was designed and constructed by Ujihara, et al.\cite{377} The principle of this device is similar to the example shown in Figure 16. The device consisted of a soft ferromagnetic material (polycrystalline Gd 99.9\%) suspended on serpentine springs near a permanent-magnet material. A permanent-magnet material with a sufficiently high Curie temperature $T_C$ was chosen because it was located adjacent to the heat source. The ambient air served as the heat sink. The authors stated that the performance of the device was 60% greater than some comparable superlattice thermoelectric generators previously reported. A similar concept but with a theoretical study was recently presented by Ahmim et al.\cite{98} Another similar concept, where the spring system is used instead of a cantilever, is shown in the Figure 17.

### 3.4. The Power of Magnetocaloric Fluids

Ferrohydrodynamics is related to the fluid motion induced by a magnetic field\cite{157} and is associated with colloidal suspensions of nanofluids. These represent fully suspended nanosized magnetic particles, where the base liquids are usually organic solvents. Because the particles are ferromagnetic, the suspensions are called ferrofluids. Therefore, we call them magnetocaloric fluids, containing fully suspended particles of magnetocaloric materials. The idea of using magnetocaloric fluids to drive turbines or apply the MHD power was not revisited after the work of researchers between 1960s and 1980s. However, magnetocaloric fluids can be used for the thermal management of devices. Namely, these fluids can be driven by a temperature gradient generated by different heat sources (i.e., electronic, photovoltaic), with the ambient air used as the heat sink. Therefore, the heat source, which requires thermal management itself, provides the energy to propel the magnetocaloric fluid, which maintains the desired temperature. The system, thus, runs autonomously. A comprehensive review of magnetocaloric fluids and their applications in energy conversion can be found the work of Kitanovski et al.\cite{35} One of the latest reviews on the application of ferrofluids in thermal management was published by Mehta et al.\cite{390} Another, more general view of the applications of ferrofluids was recently published by Zhanget et al.\cite{391}

Until 2010, only a few publications were dedicated to the use of magnetocaloric fluids in thermal management. However, this domain has been revisited and the research activities are increasing, which can also be seen by this brief review discussed below. In 2004, Love et al.\cite{392} reported a comprehensive study, where they developed and experimentally investigated a magnetocaloric pump. In the same year, Yamaguchi et al.\cite{393} numerically studied the characteristics of a thermomagnetic motor based on magnetic fluids. In 2009, Fumoto et al.\cite{394}
investigated the use of a magnetocaloric fluid for thermal management. Lian et al.\cite{195} and Xuan and Lian\cite{196} reported the application of propulsion and thermal management with a ferrofluid. They also experimentally investigated the cooling of a chip by hydrocarbon-based Mn-Zn ferrofluid and a permanent magnet with a rather small magnetic field. The authors showed that a ferrofluid cooling system results in an obvious temperature drop of the chip surface. As the heat load increases, a larger heat dissipation rate can be realized because of the stronger thermomagnetic convection, which indicates self-regulation of such a system. In 2010, Kitano et al.\cite{197} described a new idea for applying a magnetocaloric fluid for cooling a concentrated photovoltaic system. A theoretical study of a micro-pump based on the magnetocaloric effect of a magnetic fluid was performed in 2011 by Xia et al.\cite{198} Another, table-top version of the thermomagnetic pump was constructed and its performance was experimentally evaluated for two different ferrofluids by Pal et al.\cite{199} The ferrofluid flowed in a glass capillary tube 2 mm in diameter. An interesting study by Nguyen\cite{200} showed different concepts of ferrofluidic systems. In 2014, Petit et al.\cite{201} reported another experimental investigation of a ferrofluid pump for thermal management. Another work was presented by Chaudhary et al.,\cite{202} who numerically (CFD) and experimentally evaluated the principle of a ferrofluid pump with Mn-Zn ferrite nanoparticles suspended in water. Ferrofluid cooling of the heat source with 64 and 87 °C led to a decrease in the temperature by 20 and 28 K, respectively. Yamaguchi et al.\cite{203} recently developed a device-recuperator to utilize waste heat. The concentric pipe was used as a heat exchanger. To validate the operation of the ferrofluidic pump, the authors used an electromagnet. The authors used a binary fluid like a mixture of a ferrofluid and n-Hexane. The results show that the binary fluid can be circulated at high flow rates. One of the latest studies by Mehta et al.\cite{204} showed the performance of cooling by a ferrofluid in different closed-loop configurations.

4. Liquefaction of Fuels by the Magnetocaloric Effect

Energy storage\cite{205–207} is an important issue for which different strategies and technologies exist. Among these, the development of batteries\cite{208,209} certainly represents one of the major research tracks. However, hydrogen production from renewable electricity\cite{210,211} and its storage\cite{212} or pumping into power-to-gas networks\cite{213,214} also plays an important future role. The same holds for biogas or bio-methane, which may lead to future replacements for compressed natural or liquid natural gas. Hydrogen storage\cite{215} can involve storing hydrogen gas, for example, via adsorption or absorption.\cite{216,217} However, the most mature technology is actually the compression or liquefaction of hydrogen gas.\cite{218} Hydrogen liquefaction can be performed using several cryogenic methods, of which magnetic refrigeration, especially by active magnetic regeneration, is gaining increasing interest among researchers. This could also be a consequence of the greatly expanded knowledge regarding magnetocaloric refrigeration near room temperature.

Magnetocaloric materials are being applied in passive regenerators in cryogenic refrigeration technologies that are not based on the magnetocaloric effect. An overview of such magnetocaloric materials serving as passive and active magnetic regenerators in cryogenics can be found in the book of Tishin and Spichkin.\cite{219} One of the latest reviews on the different magnetocaloric materials for hydrogen and nitrogen liquefaction was conducted by Zhang et al.\cite{220} Because low-temperature magnetic refrigerators use a superconducting magnet, the following review article of Gimaev et al.\cite{221} on high-temperature superconductors in magnetic refrigeration can provide good supporting literature. After the second half of the 1960s, when dilution refrigeration reached milli-Kelvin temperatures, the application of magnetocaloric refrigeration in low-temperature physics was mostly applied in laboratories and on space missions.\cite{222} A short review of magnetic refrigeration in cryogenics up to the end of the 1990s was performed by Barclay.\cite{223} Because the aim of this article is to present work related to the energy applications of magnetocaloric materials, the subsequent text is dedicated to the liquefaction of fuels using the magnetocaloric effect. In general, two different processes can be applied in the liquefaction of fuels based on the magnetocaloric effect. The first one is adiabatic demagnetization refrigeration, which can be continuous or discontinuous. Another one is continuous active magnetic regenerative refrigeration. A special cycle was presented in 2007 by Kamiya et al.\cite{224} who provided a method for hydrogen liquefaction based on the magnetocaloric effect executing thermodynamic processes to achieve Carnot-type of refrigeration cycles. The liquefaction principle of their magnetic refrigerator was based on a thermosiphon, in which liquid hydrogen was condensed directly onto the surface of a material. Thus, the authors eliminated the losses in potential heat exchangers and increased the efficiency. The authors also developed a new ceramic polycrystal magnetic refrigerant, which they named a dysprosium-gadolinium-aluminium garnet. In their subsequent conference paper,\cite{225} the same authors presented improvements to the earlier prototype. They increased the volume fraction and changed the form of the magnetocaloric material by implementing spheres with a 0.4 mm diameter. In later publications, which will be reported in the subsequent text, the authors applied active magnetic regeneration for the precooling phase and their Carnot-like cycle in the lowest temperature-liquefaction phase.

4.1. Liquefaction of Fuels Using Adiabatic Demagnetization Refrigeration

A typical adiabatic demagnetization refrigerator (Figure 18) consists of the full body of a magnetocaloric material placed in the bore of a superconducting magnet. A connection between the magnetocaloric material and the heat sink is established using a thermal switch,\cite{226} which has been extensively researched in several investigations in the past decades.\cite{227,228,229} A typical adiabatic demagnetization cycle performs four processes. 1) The magnetocaloric material in zero field is at the heat-sink temperature with an open heat switch. 2) During the process of isothermal magnetization, the magnetic field increases until it reaches a maximum value. Simultaneously, heat from the magnetocaloric material
is constantly transferred to the heat sink through a thermal switch. 3) The heat switch is closed, and the magnetic field is reduced, leading to adiabatic cooling of the magnetocaloric material to the temperature of the heat source. 4) In the last stage, the heat is absorbed from the heat source, whereas the magnetic field decreases to its minimum value. The adiabatic demagnetization is not a regenerative cycle, nor is the magnetocaloric material in the form of a porous structure. However, different types of single-stage and multi-stage adiabatic demagnetization refrigerators can be found today, including those that have a continuous operation.[425,426] The last were developed and reported by Shirron et al.[427] Generally, adiabatic demagnetization refrigerator represents the lowest, sub-kelvin cooling stage, with its heat sink provided by other types of cryocoolers. However, the application of multi-stages allows expansion of the operation temperature interval with the heat-sink temperature well above 1 K.[428] Because adiabatic demagnetization is being replaced by the active magnetic regeneration cycle, a small number of studies can be found in the past two decades with regard to the liquefaction of fuels.

One example is the research activities of Park et al.[429,430] They presented a detailed construction of the system and the operating parameters of adiabatic demagnetization refrigerator for hydrogen re-liquefaction, operating between 24 and 20 K. In their design, a high-temperature superconducting (HTS) magnet was employed for the external magnetic field variation on the magnetocaloric refrigerant. In the experimental part of their project, the magnetocaloric material consisted of a bed of tiny irregular powders of Dy0.9Gd0.1Ni2 enclosed in a thin-walled stainless-steel container. The precooled helium traveled through the magnetic material when heat rejection was required. A flow of helium was used instead of a traditional heat switch. The conduction-cooled HTS magnet generated both strong and alternating magnetic fields from 0 to 3.0 T (0–130 A) with an average ramp rate of 0.24 T s⁻¹.

4.2. Liquefaction of Fuels by Active Magnetic Regeneration

After the important discovery of Barclay and Steyert,[156] researchers later also investigated the use of active magnetic regeneration (Figure 19) for the liquefaction of fuels.[431–433] We will here focus on the past two decades.

In 2000, Zhang et al.[434] numerically investigated the two-stage active magnetic regenerative cycle for the liquefaction of hydrogen, capable for producing 0.1 ton of liquid hydrogen per day. The two stages, consisting of GdNi2 and GdPd regenerators, were considered to operate between 77 and 20 K. A five-parameter optimization process was used for magnetocaloric regenerators. Another study on the 10 kg day⁻¹ of liquid-hydrogen production with active magnetic regeneration was presented in 2003 by Iwasaki.[435] Matsumoto et al.[436] reported on the hydrogen liquefaction, which cools down hydrogen gas from the liquid natural gas temperature and liquefies it at 20 K. The magnetic liquefaction system consisted of two magnetic refrigerators: Carnot-like magnetic refrigerator and active magnetic regenerative refrigerator. The authors also compared both cycles. In contrast, the AMR cycle was confirmed to provide a large temperature span and the Carnot-like cycle operated with higher efficiency. Hirayama[437] performed an experimental study on active magnetic regenerators consisting of GdN spherical particles of 1 mm. The refrigeration was tested in the temperature range between 48 and 66 K with a field variation from 1.2 to 3.7 T at upper side and from 2.0 to 4.0 at the lower side of the regenerator. Another study was performed by Smaili et al.[438] who developed a numerical model and theoretically investigated the first stage of hydrogen cooling for its liquefaction, that is, in the temperature range of 298–233 K. Numazawa et al.[439] in 2014 reported the development of their group in the field of liquefaction of hydrogen by magnetocaloric materials, which, as they reported, present an alternative to hydrogen liquefaction with a highly pressurized
gas. Belkadi and Smaili reported a numerical analysis\cite{440} with a multi-stage system with active magnetic regeneration, comprising six different cycles connected in series. Kwon et al.\cite{441} in their study investigated a hybrid system in which the passive regenerator of the pulse tube refrigerator was replaced by an active magnetic regenerator, composed of two different magnetocaloric materials (GdNi$_2$, Dy$_{0.85}$Er$_{0.15}$Al$_2$). Holladay et al. in 2018 reported transferring a fraction of the heat-transfer fluid into the cold heat exchangers of the active magnetic regeneration cycle.\cite{442} Because the bypassed fluid can pre-cool a process stream to the hot side, the efficiency of liquefaction can be increased. The experimental results yielded a 30% improvement in the net cooling power, compared to the ordinary operation of active magnetic regeneration. One of the rare publications on the liquefaction of other fuels than hydrogen or natural gas can be found in the recent study by Barclay et al.\cite{443} who reported the liquefaction of propane gas by applying active magnetic regeneration and an applied maximum magnetic field of 2.7 T. The tandem of Gd regenerators was provided by their movement a quasi-continuous cooling. The most recent work was reported by Teyber et al.\cite{444} who performed a comprehensive numerical study by utilizing the semi-analytical model and validated it through experimental data. In their study, the authors analyzed applying a high-field superconducting magnet. The results of the study reveal that such systems can be built for the liquefaction of natural gas. With a temperature span of 160 K, the second-law efficiency of the system was above 20%.

5. Conclusion

This article provides an overview of energy applications of magnetocaloric materials related to numerous different energy-conversion technologies, that is, refrigeration, heat pumping, air-conditioning, heat-to-power energy conversion, and the liquefaction of fuels. This highly interdisciplinary domain merges natural and engineering sciences, thus representing a complex research field, which still requires large research efforts for real, market-available applications. As can be seen from the cited literature, a large part of the research activities belongs to the past 10–20 years. The research in magnetocaloric refrigeration and heat pumping certainly means it has a future position in the market. Therefore, it will be important to implement different ways of thinking and overcome the main barriers that concern not only substantial improvements in the magnetocaloric and mechanical as well as the thermal properties of materials but which also concern their availability, recycling, cost, and environmental impact. The last of these also concerns magnetic field sources, for which the latest activities show directions that may bring concepts without rare-earth materials. Moreover, the implementation of new and future knowledge in thermal control elements, which have the potential to substantially increase the power density of present devices, can drastically affect the development not only of magnetic refrigerators and heat pumps, but also of power generators. For these devices, we are currently witnessing the first conceptual prototypes that operate with a very low power density, sometimes also a very low efficiency. Nevertheless, these prototype devices show characteristics for harvesting low-grade thermal sources, for which other technologies cannot be efficiently applied. The production of liquefied fuels is one of the domains where we have witnessed substantial improvements in magnetocaloric refrigeration in the last 20 years. Therefore, in the future applications of magnetocaloric materials, perhaps we will see them play a role in energy transport and storage and in the creation of environmentally friendly and sustainable future fuels.

Besides a comprehensive review of past and present activities in the energy application of magnetocaloric materials, this article hopefully provides sufficient background to encourage new scientists and engineers to play a part in the future of magnetocalorics. It can also serve to provide important future directions for experts working in different fields related to magnetocaloric materials or their applications.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The author acknowledges the financial support of the Slovenian Research Agency for the project Multicaloric cooling J2-9253 and the research program Heat and Mass transfer P2-0223.

Conflict of Interest

The author declares no conflict of interest.

Keywords

energy conversion, heat pumps, magnetocalorics, refrigeration, thermomagnetics

Received: November 13, 2019
Revised: December 30, 2019
Published online: February 3, 2020

[1] D. Coulomb, J. L. Dupont, A. Pichard, The Role of Refrigeration in the Global Economy, 29th Informatory Note on Refrigeration Technologies, Technical Report, International Institute of Refrigeration, Paris, France 2015.

[2] International Energy Agency, The Future of Cooling, 2018, http://www.iea.org/reports/the-future-of-cooling, (accessed: November 2019).

[3] J. S. Brown, P. A. Domanski, Appl. Therm. Eng. 2014, 64, 252.

[4] B. Y. W. Goetzler, M. Ashrae, R. Zogg, M. Ashrae, J. I. M. Young, A. M. Ashrae, C. Johnson, A. M. Ashrae, ASHRAE J. 2014, 12.

[5] D. R. Brown, T. B. Stout, J. A. Dirks, N. Fernandez, Energy Eng. 2012, 109, 7.

[6] P. A. Domanski, J. Steven Brown, J. Heo, W. Jeo, W. Jeo, M. O. McLinden, Int. J. Refrig. 2014, 38, 71.

[7] C. O. R. Negrão, C. J. L. Hermes, Appl. Energy 2011, 88, 3051.

[8] S. Choi, U. Han, H. Cho, H. Lee, Appl. Therm. Eng. 2018, 132, 560.

[9] D. Coulomb, J.-L. Dupont, V. Morlet, The Impact of the Refrigeration Sector on Climate Change, 35th Informatory Note on Refrigeration Technologies, Technical Report, International Institute of Refrigeration, Paris, France 2017.

[10] Y. Hwang, Harmonization of the Life Cycle Climate Performance Methodology, 32nd Informatory Note on Refrigeration Technologies, Technical Report, International Institute of Refrigeration, Paris, France 2016.

[11] I. H. Bell, P. A. Domanski, M. O. McLinden, G. T. Linteris, Int. J. Refrig. 2019, 104, 484.

[12] P. A. Domanski, R. Brigioni, J. S. Brown, A. F. Kazakov, M. O. McLinden, Int. J. Refrig. 2017, 64, 198.

[13] M. O. McLinden, J. S. Brown, R. Brigioni, A. F. Kazakov, P. A. Domanski, Nat. Commun. 2017, 8, 14476.

[14] International Institute of Refrigeration, http://www.iiifir.org/userfiles/file/webfiles/registration_files/Synthèse_Kigali_EN.pdf (accessed: November 2019).

[15] E. Clark, S. Wagner, The Kigali Amendment to the Montreal Protocol: HFC Phase-Down, OzonAction UN Environment (UNEP), Paris, France 2016.

[16] S. Qian, D. Nasuta, A. Rhoods, Y. Wang, Y. Geng, Y. Hwang, R. Radermacher, I. Takeuchi, Int. J. Refrig. 2016, 62, 177.

[17] W. Goetzler, M. Guernsey, J. Young, J. Fuhrman, O. Abdelaliz, The Future of Air Conditioning for Buildings, US Department of Energy, Energy Efficiency & Renewable Energy, Building Technologies Office, Washington, DC 2016.

[18] M. Hamdy, A. A. Askalany, K. Harby, N. Kora, Renewable Sustainable Energy Rev. 2015, 51, 1223.

[19] P. S. Arshi Banu, N. M. Sudharsan, Renewable Sustainable Energy Rev. 2018, 82, 3750.

[20] D. S. Ayu, J. C. Bruno, R. Saravanavan, A. Coronas, Renewable Sustainable Energy Rev. 2013, 21, 728.

[21] A. Shirazi, R. A. Taylor, G. L. Morrison, S. D. White, Energy Convers. Manage. 2018, 171, 59.

[22] B. M. Tashtoush, M. A. Al-Nimr, M. A. Khasawneh, Appl. Energy 2019, 240, 138.

[23] G. Besagni, R. Mereu, F. Inzoli, Renewable Sustainable Energy Rev. 2016, 53, 373.

[24] D. Enescu, E. O. Virgohge, Renewable Sustainable Energy Rev. 2014, 38, 903.

[25] I. Sarbu, A. Dorca, Int. J. Energy Res. 2018, 42, 395.

[26] R. A. Kishore, A. Nozariasbmarz, B. Poudel, M. Sanghadasa, S. Priya, Nat. Commun. 2019, 10, 1765.

[27] G. Li, J. Garcia Fernandez, D. A. Lara Ramos, V. Barati, N. Pérez, I. Soldatov, H. Reith, G. Schiering, K. Nielsch, Nat. Electron. 2018, 1, 555.

[28] Y. Cai, Y. Wang, D. Liu, F. Y. Zhao, Appl. Therm. Eng. 2019, 148, 238.

[29] L. K. Tartibu, Sustainable Energy Technol. Assess. 2019, 31, 102.

[30] N. A. Zolpakar, M. Mohd-Ghazali, M. Hassan El-Fawal, Renewable Sustainable Energy Rev. 2016, 54, 626.

[31] A. Kitanovski, U. Plaznik, U. Tomc, A. Poredoš, Int. J. Refrig. 2015, 57, 258.

[32] X. Moya, S. Kar-Narayan, N. D. Mathur, Nat. Mater. 2014, 13, 439.

[33] X. Moya, E. Defay, V. Heine, N. D. Mathur, Nat. Phys. 2015, 11, 202.

[34] A. Barman, S. Kar-Narayan, D. Mukherjee, Adv. Mater. Interfaces 2019, 6, 1900291.

[35] A. Kitanovski, J. Tušek, U. Tomc, U. Plaznik, M. Ožbolt, A. Poredoš, Magnetocaloric Energy Conversion–From Theory to Applications, Springer, Basel, Switzerland 2015.

[36] V. Franco, J. S. Blázquez, J. J. Ipus, J. V. Law, L. M. Moreno-Ramirez, A. Conde, Prog. Mater. Sci. 2018, 93, 112.

[37] T. Gottschall, K. P. Skokov, M. Fries, A. Taubel, I. Radulov, F. Scheibef, D. Benke, S. Riegel, O. Gutfleisch, Adv. Energy Mater. 2019, 9, 1901322.

[38] J. Shi, D. Han, Z. Li, L. Yang, S. G. Lu, Z. Zhong, J. Chen, Q. M. Zhang, X. Qian, Joule 2019, 3, 1200.

[39] M. Ožbolt, A. Kitanovski, J. Tušek, A. Poredoš, Int. J. Refrig. 2014, 40, 174.

[40] C. Aprea, A. Greco, A. Maiorino, C. Masselli, J. Phys.: Cond. Ser. 2017, 796, 012019.

[41] F. Brueiderlin, L. Bumke, C. Chiluba, H. Ossmer, E. Quandt, M. Kohl, Energy Technol. 2018, 6, 1588.

[42] L. Mašosa, A. Planes, Adv. Mater. 2017, 29, 1603067.

[43] J. Tušek, K. Engelbrecht, R. Millán-Solsona, L. Mašosa, E. Vives, L. P. Mikkelsen, N. Prlys, Adv. Energy Mater. 2015, 5, 1500361.

[44] T. Gottschall, A. Gràcia-Condal, M. Fries, A. Taubel, L. Pfeuffer, L. Mašosa, A. Planes, K. P. Skokov, O. Gutfleisch, Nat. Mater. 2018, 17, 929.

[45] U. Ursic, V. Bobnar, B. Malic, C. Filipic, M. Vrablj, S. Drnovšek, Y. Jo, M. Wencka, Z. Kutnjak, Sci. Rep. 2016, 6, 26629.

[46] A. Planes, T. Castán, A. Saxena, Philos. Trans. R. Soc., A 2016, 374, 20150304.

[47] C. Forman, I. K. Muritala, R. Pardemann, B. Meyer, Renewable Sustainable Energy Rev. 2016, 57, 1568.

[48] H. Jouhara, N. Khordehghah, S. Almahmoud, B. Delpech, A. Chauhan, S. A. Tassou, Therm. Sci. Eng. Prog. 2018, 6, 268.
[392] L. J. Love, J. F. Jansen, T. E. McKnight, Y. Roh, T. J. Phelps, IEEE Trans. Nanosci. 2004, 3, 101.
[393] H. Yamaguchi, A. Sumijii, S. Shuchi, T. Yonemura, J. Magn. Magn. Mater. 2004, 272–276, 2362.
[394] K. Fumoto, M. Ikegawa, T. Kawanami, J. Therm. Sci. Technol. 2009, 4, 332.
[395] W. Lian, Y. Xuan, Q. Li, Int. J. Heat Mass Transfer 2009, 52, 5451.
[396] Y. Xuan, W. Lian, Appl. Therm. Eng. 2011, 31, 1487.
[397] C. Xia, T. Liu, X. Qin, X. Zou, Z. Qian, in Proc. of the Second Int. Conf. on Mechanic Automation and Control Engineering (MACE 11), IEEE, Piscataway, NJ 2011, pp. 5192–5195.
[398] S. Pal, A. Datta, S. Sen, A. Mukhopadhyay, K. Bandopadhyay, R. Ganguly, J. Magn. Magn. Mater. 2011, 323, 2701.
[399] N. T. Nguyen, Microfluid. Nanofluid. 2012, 12, 1.
[400] M. Petit, Y. Avenas, A. Kedous-Lebouc, W. Cherief, E. Rulliere, Int. J. Refrig. 2014, 37, 201.
[401] V. Chaudhary, Z. Wang, A. Ray, I. Sridhar, R. V. Ramanujan, J. Phys. D: Appl. Phys. 2017, 50, 03LT03.
[402] H. Yamaguchi, H. Yamasaki, T. Bessho, Proc. Inst. Mech. Eng., Part C 2019, 233, 4754.
[403] J. S. Mehta, R. Kumar, H. Kumar, H. Garg, J. Phys.: Conf. Ser. 2019, 1240, 012056.
[404] N. Khan, S. Dilshad, R. Khalid, A. R. Kalair, N. Abas, Energy Storage 2019, 1, e49.
[405] S. Hameer, J. L. van Niekerk, Int. J. Energy Res. 2015, 39, 1179.
[406] O. Krishan, S. Suhaq, Int. J. Energy Res. 2019, 43, 6171.
[407] S. Comello, S. Reichelstein, Nat. Commun. 2019, 10, 2038.
[408] Nature Reviews Materials, Battery Materials and Technologies, https://www.nature.com/collections/rjplyqvvhr (accessed: November 2019).
[409] J. Qi, W. Zhang, R. Cao, Adv. Energy Mater. 2018, 8, 1701620.
[410] S. E. Hosseini, M. Abdul Wahid, M. M. Jamil, A. A. Azli, M. F. Gainsb, Int. J. Energy Res. 2015, 39, 1597.
[411] P. Adametz, C. Pöttinger, S. Müller, K. Müller, M. Preißinger, R. Lechner, D. Brüggemann, M. Brautsch, W. Arlt, Energy Technol. 2017, 5, 495.
[412] T. N. Russo, Nat. Gas Electr. 2019, 36, 25.
[413] A. Ajanovic, R. Haas, Wiley Interdiscip. Rev.: Energy Environ. 2019, 8, e318.
[414] C. Bourasseau, B. Guinot, in Hydrogen Production: By Electrolysis (Eds: A. Godula-Jopek, D. Stolten), Wiley-VCH, Weinheim, Germany 2015, p. 311.
[415] M. Mohan, V. K. Sharma, E. A. Kumar, V. Gayathri, Energy Storage 2019, 1, e35.
[416] J. Andersson, S. Grönkvist, Int. J. Hydrogen Energy 2019, 44, 11901.
[417] A. Alekseyev, in Hydrogen Science and Engineering: Materials, Processes, Systems and Technology (Eds: D. Stolten, B. Emonts), Wiley, New York 2016, p. 733.
[418] H. Zhang, R. Gimaev, B. Kovalev, K. Kamilov, V. Zverev, A. Tishin, Phys. B 2019, 558, 65.
[419] P. J. Shirron, J. Low Temp. Phys. 2007, 148, 915.
[420] J. A. Barclay, in Advances in Cryogenic Engineering (Ed: R. W. Fast), Springer, Boston, MA 1988, pp. 719–731.
[421] K. Kamiya, H. Takahashi, T. Numazawa, H. Nozawa, T. Yanagitani, in Proc. of the 14th Int. Cryocooler Conf. (Eds: S. D. Miller, R. G. Ross Jr.), International Cryocooler Conference, Boulder 2007, pp. 637–644.
[422] K. Kamiya, T. Numazawa, K. Matsumoto, S. Abe, H. Nozawa, T. Yanagitani, AIP Conf. Proc. 2008, 850, 1583.
[423] Y. Ishisaki, K. Henmi, H. Akamatsu, T. Enoki, T. Ohashi, A. Hoshino, K. Shinozaki, H. Matsuo, N. Okada, T. Oshima, J. Low Temp. Phys. 2012, 167, 777.
[424] J. Bartlett, G. Hardy, I. D. Hepburn, Cryogenics 2015, 72, 111.
[425] P. J. Shirron, Cryogenics 2014, 62, 130.
[426] P. J. Shirron, Cryogenics 2014, 62, 140.
[427] P. J. Shirron, E. R. Canavan, M. J. Dipirro, G. Tuttle, C. J. Yeager, Advances in Cryogenic Engineering (Ed: Shu et al.), Springer, Boston, MA 2000, 45, 1629.
[428] J. Tuttle, E. Canavan, H. Delee, M. Dipirro, T. James, M. Kimball, P. Shinnor, D. Sullivan, E. Switzer, IOP Conf. Ser.: Mater. Sci. Eng. 2017, 278, 012009.
[429] J.-H. Park, Y.-K. Kim, S.-K. Jeong, S.-H. Kim, Prog. Supercond. Cryogenics 2012, 14, 53.
[430] J. Park, S. Jeong, I. Park, Cryogenics 2015, 71, 82.
[431] Astronautics Corporation of America, Magnetic Liquefier for Hydrogen, Astronautics Corporation of America, Madison, WI 1992.
[432] A. J. DeGregoria, L. J. Feuling, J. F. Laatsch, J. R. Rowe, J. R. Trueblood, A. A. Wang, in Advances in Cryogenic Engineering (Ed: R. W. Fast), Springer, Boston, MA 1992, pp. 875–882.
[433] F. J. Cogswell, J. L. Smith Jr., Y. Iwasa, in Proc. of the 5th Int. Cryocooler Conf. (Eds: P. Lindquist, A. Johnson), International Cryocooler Conference, Boulder 1988, pp. 637–644.
[434] L. Zhang, S. A. Sherif, A. J. DeGregoria, C. B. Zimm, T. N. Veziroglu, Cryogenics 2000, 40, 269.
[435] W. Iwasaki, Int. J. Hydrogen Energy 2003, 28, 559.
[436] K. Matsumoto, T. Kondo, S. Yoshioka, K. Kamiya, T. Numazawa, J. Phys.: Conf. Ser. 2009, 150, 012028.
[437] Y. Hirayama, H. Okada, T. Nakagawa, T. A. Yamamoto, T. Kusunose, T. Numazawa, K. Mastumoto, T. Irie, E. Nakamura, in Cryocoolers 16, 2011, pp. 531–536.
[438] A. Smalli, S. Alt-Al, R. Chahine, Int. J. Hydrogen Energy 2011, 36, 4169.
[439] T. Numazawa, K. Kamiya, T. Utaki, K. Matsumoto, Cryogenics 2014, 62, 185.
[440] M. Belkadi, A. Smalli, Int. J. Hydrogen Energy 2018, 43, 3499.
[441] D. Kwon, I. Park, S. Jeong, W. Åxdg, D. O. G. Lwv, R. Arz, 2. V Dflkhyhg, E. D. K. Frpsuhvvru, D. Q. G. Wzr, V. Ydoyhv, in Cryocoolers 20, 2018, pp. 263–270.
[442] J. Holladay, R. Teyber, K. Meinhardt, E. Polikarpov, E. Thomsen, C. Archipley, J. Cui, J. Barclay, Cryogenics 2018, 93, 34.
[443] J. Barclay, K. Brooks, J. Cui, J. Holladay, K. Meinhardt, E. Polikarpov, E. Thomsen, Cryogenics 2019, 100, 69.
[444] R. Teyber, J. Holladay, K. Meinhardt, E. Polikarpov, E. Thomsen, J. Cui, A. Rowe, J. Barclay, Appl. Energy 2019, 236, 426.