18.1 Introduction

The ability to induce a reversible temperature change in a magnetic material by changing the magnetization is called the magnetocaloric effect (MCE) and has been known for over 100 years. Magnetic cooling is a process that uses the MCE to reduce the temperature of another substance and was originally employed to produce temperatures lower than those possible with liquid helium (LHe). Since the early 1970s, advancements in materials (magnetic refrigerants, superconductors, permanent magnets) and our understanding of the thermodynamics of magnetic cycles have led to increased interest in using magnetic cycles for a variety of applications. One area of particular interest is the liquefaction of hydrogen. Although no commercial liquefiers using the MCE currently exist, the potential for high efficiencies at smaller scales and lower cost than conventional gas expansion cycles is a driver of research and development activities. In addition, future energy systems in which hydrogen is used as an energy carrier require logistical chains for transmission, distribution, and storage. For this to happen, the need for hydrogen liquefaction will grow substantially from current levels.

This chapter describes some of the activities reported in the literature regarding magnetic liquefaction of hydrogen. A brief history of magnetic refrigeration is provided and is followed by a summary of the basic thermodynamic relationships quantifying the performance of magnetocaloric materials and cycles. Following this, there is a review of proposed devices and their configurations. Some of the refrigerants that have been specifically suggested for use in hydrogen liquefaction will be discussed, but, given the substantial research currently happening on material synthesis and characterization, no attempt will be made to cover this area rigorously. Instead, the reader will be directed to reviews where further information can be found. Likewise, much of the work on device development has been in national laboratories and companies through government contract research. Many of the details for these projects are not easily accessible; thus, this review will focus on information available in the open literature.

18.1.1 Overview of Magnetic Refrigeration

Magnetic refrigeration is based upon a phenomenon known as the MCE. The MCE is sometimes described as the isothermal entropy change due to a change in the applied magnetic field. In order to produce useful cooling or heat with a magnetic material, there must be a decrease or increase in temperature due to a change in the applied field—this is the adiabatic temperature change and is another way of reporting the MCE. Unlike eddy-current heating, the MCE is identified by the reversible change in temperature when adiabatically subjected to a magnetic field. For a given material, the magnitude of this temperature change is proportional to the strength of the applied magnetic field. Different materials also display this effect to varying degrees depending upon properties such as the Curie temperature, magnetic entropy, and lattice entropy.

Using the MCE, it is possible to form a cycle that parallels a vapor-compression process whereby a volume can be continuously refrigerated through a cyclical process. The compression and expansion stages of a gas-refrigeration system are replaced by magnetizing and demagnetizing a magnetic material. Because the working substance is a solid with limited heat transfer capabilities, a heat transfer fluid is used to thermally couple the refrigerant to hot and cold heat sinks. An example of a particular process for a magnetic refrigeration cycle is summarized in the following paragraph with reference to Figure 18.1.
When a conventional magnetocaloric material is reversibly subjected to a magnetic field change, the magnetic dipoles become more ordered. In practice, this can be observed by measuring the force on a substance in a nonuniform magnetic field. If the total entropy is to remain constant, adiabatic magnetization causes magnetic entropy to decrease, which results in an increase in temperature of the lattice. With the magnetic field still applied, the adiabatic condition is relaxed so that the material rejects heat and the temperature decreases. Next, an adiabatic condition is imposed, the magnetic field is then removed so that the magnetic order decreases, and the temperature decreases below its original value. Once again, the material is thermally coupled to absorb heat and the material returns to the original state, completing the cycle.

While all magnetic refrigeration cycles utilize the same basic steps, the actual cycle depends on the application (temperature span and cooling power) and available refrigerants. In addition, device geometries and heat transfer flow configurations can be quite different.

Although the MCE was hypothesized to exist by Kelvin [1] and measured by Weiss and Piccard [2] in 1918, magnetic cooling was not demonstrated until 1933 [3,4]. The idea of using the MCE for hydrogen liquefaction did not appear until the late 1970s.

The first applications of magnetic cooling were to produce sub-Kelvin temperatures with a single-shot process where the entire mass of refrigerant was brought to a uniform temperature and demagnetized. Larger amounts of material could cool more mass and maintain low temperatures for longer periods. For paramagnetic materials at low temperatures, the total entropy of the refrigerant is dominated by the magnetic entropy and, therefore, significant temperature changes are easy to produce. At higher temperatures,
the magnetic entropy change in a paramagnetic material becomes insignificant relative to the total entropy, making the temperature change small. The primary deterrent to high-temperature cooling was thought to be a lack of materials, which showed a significant temperature change when a moderate magnetic field (0–7 T) was applied.

In the mid-1970s, two important developments for magnetic refrigeration were reported by Brown: (1) a ferromagnetic material near its Curie temperature was used to produce a similar effect to that of the paramagnetic salts and (2) the limitations of the MCE were overcome using recuperation. Shortly after this work, the use of ferromagnetic materials for magnetic refrigeration in the range of 10 K to room temperature was described [5].

Brown demonstrated a magnetic refrigerator producing a temperature span of 47°C using gadolinium [6], and it was the first time that magnetic refrigeration was demonstrated at temperatures above 20 K. Brown’s experimental testing was discussed by Steyert [7] who analyzed the reversibility of magnetic refrigeration. He concluded that continued progress should allow for magnetic refrigeration to have higher efficiencies than existing gas-refrigeration technologies. Perhaps the most significant development for magnetic refrigeration at temperatures above 20 K was the idea of using the magnetocaloric material in the form of a regenerator. This idea was called an active magnetic regenerator (AMR) and was patented by Barclay and Steyert [8]. In addition to using regeneration, the AMR concept overcomes the limited range of a single magnetocaloric material by using a number of different materials in a layered structure. Similar to a passive regenerator, the solid matrix periodically exchanges heat with a fluid oscillating through the pores. Unlike a passive regenerator, however, the solid refrigerant is the working material that creates the temperature distribution from the hot end to the cold end. Today, nearly all MR development above 20 K is making use of the AMR concept.

These initial papers subsequently led to several studies regarding magnetic materials, device design, and analytic studies of performance [9–12].

18.1.2 History of Magnetic Liquefaction of Hydrogen

The idea of using magnetic cycles for hydrogen liquefaction really started at the beginning of the 1980s. During 1982–1986, a number of related studies were performed by a group at Los Alamos National Laboratory [13]. The work was primarily funded by NASA and various offices in the US DOE. Hydrogen reliquefaction using a magnetic refrigerator was one application, and the development of a device operating between liquid nitrogen (LN$_2$) and liquid hydrogen was another. The latter was identified as having good commercialization potential due to the significant fraction of capital expenditures required for the 77–20 K range with conventional liquefiers [14]. A number of devices were designed, analyzed, and tested; details of those designed to work below LN$_2$ will be discussed later.

In 1991, Barclay summarized the status of magnetic refrigeration technology and discussed the future prospects for liquefaction of hydrogen [15]. This summary explained the technical aspects of magnetic refrigeration in addition to describing the thermodynamic advantages they have over conventional systems. The regenerator was identified as being the main design challenge to create a magnetic device spanning 300–20 K. This chapter concluded with a cost estimate of two different magnetic liquefiers operating from 77 to 20 K, indicating the potential for significantly lower cost than a gas-cycle device. In 1992, Janda et al. [16] reported the design of a 0.1 ton/day AMR refrigerator for liquefying hydrogen; this device was later analyzed by Zimm et al. [17] and Degregoria [18]. This study of this design was continued by Zhang et al. in 2000 in the form of an optimization study [19]. The most recent design and experimental unit was created by Kamiya et al. [20].
and Matsumoto et al. [21], which takes into account the actual condensation process of hydrogen using a Carnot magnetic refrigerator (CMR) stage.

The potential for magnetic refrigeration to be used in hydrogen liquefaction has made the 77–20 K range a focus for magnetic refrigeration. Multiple papers have now been dedicated to theoretical studies [22,23], numerical models [24–32], test devices [33–37], and review articles [38,39] in an effort to improve the process of hydrogen liquefaction and make magnetic liquefaction a competitive alternative to traditional gas expansion cycles.

The thermodynamics of the MCE is introduced in the following section and leads to a discussion of magnetic cycles.

18.2 Thermodynamics

This section discusses the fundamental theory and processes behind magnetic refrigeration. This includes the functional form for quantifying magnetic work, entropy, and specific heat. The basic cycles of magnetic refrigeration such as the Carnot, Stirling, Ericsson, and Brayton cycles are then reviewed. The AMR cycle is also described followed by a brief summary of some of the losses that limit magnetic cycle performance.

18.2.1 Magnetic Systems

The following sections review the fundamental thermodynamic quantities of a material with a reversible magnetic work mode. For simplicity, it is assumed that the material has no significant volume change, is homogenous and hysteresis-free, and has continuous specific heat as a function of field and temperature. Materials that fit these assumptions well are some of the rare-earth elements and alloys and materials displaying a second-order magnetic phase change. A number of first-order materials have good potential as magnetic refrigerants; however, their behavior tends to be more complicated than second-order materials. For those interested readers, more details on magnetocaloric materials can be found in the literature [40,41].

A challenge one encounters when dealing with magnetism, magnetic fields, and magnetocaloric materials is the wide range of units and potentials one can work with. Here we will work with the following symbols and magnetic quantities: $B_0$ is the flux density applied to a material and is considered to be due to the magnetic field, $H_\text{in}$ generated by a coil in free space. The magnetism of a material, $M$, is assumed to be a single-value function of temperature, $T$, and $H$. A significant amount of confusion (and error) can arise when discussing the magnetic field because the field in a body is generally not the same as the applied field and depends upon the shape of the material. The impact of shape on magnetization is often accounted for by a demagnetizing field, $H_\text{d}$. The local field determines the local magnetization, and the local internal field in a magnetic material is $H_i = H_0 + H_\text{d}$. Fields, fluxes, and magnetizations are vectors, but, for thermodynamic considerations, we will assume that all values are 1D.

18.2.1.1 Work

By strategically applying and removing a magnetic field to a magnetocaloric material, it is possible to develop a process that extracts heat from a cold environment and rejects it to a
hot environment. The act of magnetizing and demagnetizing a material parallels that of compressing and expanding a gas and, similarly, is achieved by a work interaction.

The first law of thermodynamics relates the energy change in a magnetic material to heat transfer and magnetic work:

\[ du = dq + dw. \]  

(18.1)

In the previous texts, the work and heat transfer are assumed to be in the material system. A clear derivation of the appropriate generalized force and displacement for a magnetic system can be found in Appendix B of [42]. One can differentiate between work done by a power supply to generate a magnetic field and the work that changes the internal energy of the material. The latter is the magnetic work and the incremental value per unit volume of material is

\[ dw = B_0 dM = \mu_0 H_0 dM, \]  

(18.2)

where \( \mu_0 \) is the permeability of free space. The applied field is analogous to the generalized force, and the magnetization (total magnetic moment per unit volume) is the generalized displacement. One can now see how the work done on magnetic material compares to that done in gas refrigeration by observing the fundamental relation of a simple compressible system:

\[ du = dq - pdv. \]  

(18.3)

Other potentials for magnetic systems can be derived using Maxwell’s relationships [43,44].

### 18.2.1.2 Entropy

The entropy of a magnetic material can be introduced into Equation 18.1 by replacing the differential heat transfer with the entropy equivalent. The entropy of a simple magnetic material is a function of temperature and field strength, \( s = s(T, H) \), and the differential change is

\[ \frac{dq}{T} = ds = \left( \frac{\partial s}{\partial T} \right)_H dT + \left( \frac{\partial s}{\partial H} \right)_T dH. \]  

(18.4)

The first term in Equation 18.4 can be replaced using the definition of specific heat at constant field, \( c_H \)

\[ c_H \equiv \left( \frac{\partial s}{\partial T} \right)_H T. \]  

(18.5)

The last term in Equation 18.4 can be written in terms of magnetization and temperature using Maxwell’s relations,

\[ \left( \frac{\partial M}{\partial T} \right)_H = \left( \frac{\partial s}{\mu_0 \partial H} \right)_T. \]  

(18.6)
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So, the variation in entropy due to temperature and field change is

\[ ds = \frac{c_H}{T} dT + \left( \frac{\partial M}{\partial T} \right)_{H} \mu_0 dH_0. \]  

(18.7)

Magnetization can be estimated by model calculations (i.e., molecular field theory) or by direct measurement.

The total entropy of the material can also be broken down into a summation of the lattice entropy \( s_g \), magnetic entropy \( s_m \), and entropy from conducting electrons \( s_E \):

\[ s_{tot} = s_m + s_E + s_g. \]  

(18.8)

Standard expressions can be used to quantify the lattice and electronic contributions to entropy (such as the Debye approximation for the lattice and quantum theory for a free-electron gas [45]). The isothermal change in magnetic entropy as a result of the applied magnetic field is determined by integrating Equation 18.7:

\[ \Delta s_{m}(T, H) = \int_{0}^{H} \left( \frac{\partial M}{\partial T} \right)_{H} \mu_0 dH. \]  

(18.9)

The isothermal magnetic entropy change is often called the MCE, but this is a derived quantity, whereas the adiabatic temperature change can be directly measured.

A reversible adiabatic process implies constant entropy; therefore, using Equation 18.7, the adiabatic temperature change can be calculated from specific heat and magnetization data as

\[ \Delta T = -\int_{0}^{H} \frac{T}{c_H} \left( \frac{\partial M}{\partial T} \right)_{H} \mu_0 dH. \]  

(18.10)

Thus, the dependence of adiabatic temperature change on magnetic entropy change is determined by the variation in specific heat with temperature.

The magnitude of the change in entropy, and the temperature change, is dependent upon the material and the operating temperature. At a certain point known as the Curie temperature, \( T_C \), the MCE is a maximum. As a material is cooled below the Curie point, the material spontaneously magnetizes (orders) and displays properties similar to ferromagnetic materials. As the temperature rises above the Curie point, the dipoles become randomized again and the response to a magnetic field is more similar to a paramagnet. Every material has a distinct Curie temperature based upon its internal magnetic and crystal structure.

The relationship between adiabatic temperature change and isothermal magnetic entropy change for gadolinium is shown in Figure 18.2a. Gadolinium is a good prototype refrigerant ordering near room temperature. Figure 18.2b shows that the MCE decreases quickly as the temperature deviates from the Curie point. As will be discussed later, this characteristic limits the use of magnetic cooling using traditional cycles.
The impact of magnetization on specific heat can be shown using Equation 18.7. Noting that this is the total differential of entropy, the following result can be derived due to equivalence of the second partial derivatives [39]:

$$c_H(T, H) = c_0(T, 0) + T \int_0^H \left( \frac{\partial^2 M}{\partial T^2} \right)_0 \mu_0 dH.$$  \hspace{1cm} (18.11)

It can be seen that the heat capacity of the magnetic material is dependent upon the variation in magnetization with field and temperature. Near the Curie temperature, specific heat can be a strong function of field and temperature. This behavior complicates modeling and optimal operating strategies.

An overview of magnetic cycles is presented in the following section. The cycle currently favored for magnetic refrigeration is an AMR. As no single material has the ideal properties for this type of process, there is a substantial research effort in the materials science community aimed at developing materials. Magnetic refrigerants for hydrogen liquefaction will be discussed following the overview of cycles.

### 18.2.2 Magnetic Refrigeration Cycles

Although all magnetic refrigeration processes make use of the same basic physical response, idealized processes can be defined depending upon how and when heat transfer
and field changes occur. This section will introduce the current cycles used in magnetic refrigeration processes and discuss the fundamental differences between them.

The primary cycles used with fluids are the classical thermodynamic cycles, that is, Brayton, Ericsson, and Stirling. Analogous cycles can be defined for magnetic solids where magnetization and field replace volume and pressure, respectively. The Carnot cycle quantifies the maximum performance of a cycle using isothermal heat rejection and absorption. An important consideration is that a Carnot cycle is not the most efficient process for gas liquefaction where sensible heat must be removed in addition to latent heat. This will become evident later when discussing proposed processes for hydrogen liquefaction.

### 18.2.2.1 Carnot Cycle

A magnetic Carnot cycle is composed of the four reversible processes shown in Figure 18.3:

1. (1–2): Adiabatic magnetization of the magnetic refrigerant
2. (2–3): Isothermal heat rejection
3. (3–4): Adiabatic demagnetization
4. (4–1): Isothermal heat addition

In adiabatic magnetization (1–2), the temperature of the material is increased isentropically due to an increase in the magnetic field. The magnetic field is then further increased while the magnetic refrigerant rejects heat to keep the material isothermal (2–3). In actuality, this continuous cooling effect would take a large heat exchanger and a large period of time, both of which are not ideal with respect to cost. With thermal isolation restored, the material is adiabatically cooled (3–4) by partially removing the magnetic field. The final step absorbs heat while simultaneously reducing the magnetic field (4–1).

In Figure 18.3, the net magnetic work, $w$, required in the cycle is equal to the area of the $T$-$s$ diagram bounded by (1–2–3–4). Similarly, the cooling capacity, $q_c$, is the area underneath

![FIGURE 18.3](https://example.com/figure18.3)

the Carnot cycle, which is (a–b–1–4). The coefficient of performance (COP) that describes the efficiency of a refrigerator can then be found:

\[
\text{COP}_R = \frac{q_c}{w} = \frac{T_1}{T_2 - T_1}.
\]

This COP acts as an upper bound for the other refrigeration cycles as each of the four processes is reversible. Since isothermal processes are used, the cooling capacity per unit work is maximized. A disadvantage of the isothermal processes, however, is the reduced temperature spans available for a given magnetic field as compared to other cycles. This can be seen by considering Figure 18.2. The maximum span of a Carnot cycle is constrained by the total entropy curves at high field and low field. In the case of gadolinium using a high field, a Carnot cycle could only operate over spans on the order of 10 K.

### 18.2.2.2 Brayton Cycle

The Brayton cycle is a more practical cycle for substances not utilizing a first-order phase change as, in practice, it is easier to do. This cycle is composed of two adiabatic processes and two processes where heat is transferred under a constant magnetic field. This is summarized as follows:

1. (1–2): Adiabatic magnetization
2. (2–3): Heat rejection with a constant magnetic field, \( H_0^{(2)} \)
3. (3–4): Adiabatic demagnetization
4. (4–1): Heat addition with a constant magnetic field, \( H_0^{(1)} \)

A T-s diagram of the ideal magnetic Brayton cycle is provided in Figure 18.4. This ideal cycle ignores the irreversibilities associated with each process.

**FIGURE 18.4**
The work done by the magnetic material can be found by calculating the area defined by the process (1–2–3–4) while the heat removed from the working fluid is equal to the area under the cycle (a–b–1–4). In actual cycles, losses of efficiency will occur in the adiabatic magnetization (1–2) and demagnetization (3–4) processes due to an irreversible entropy change.

In theory, with an equivalent effective temperature span, the magnetic Brayton cycle sacrifices efficiency as compared to Carnot. Less heat is absorbed per cycle and more work is inputted; however, this neglects thermal resistances between the heat sinks in a Carnot cycle. For a material like gadolinium with a 10 T field change, the temperature span is about 15–20 K compared to the 5–10 K/10 T temperature change for the Carnot cycle [6]. This is because the heat transfer is done with a constant magnetic field instead of isothermally, resulting in a larger change in the magnetic field in the isentropic processes. A larger temperature range could be obtained by maintaining the isothermal processes of the Carnot cycle but regenerating heat under a constant magnetic field; this is the foundation for the Ericsson and Stirling cycles.

18.2.2.3 Ericsson and Stirling Cycles

The Ericsson and Stirling cycles are very similar to one another from an energy standpoint. These cycles both utilize the isothermal heat transfer of the Carnot cycle and both require heat regeneration to be considered ideal. The adiabatic magnetizing and demagnetizing of the material is however replaced by a constant magnetic field strength, $H$, in the Ericsson cycle and constant magnetization, $M$, in the Stirling cycle. The Ericsson cycle is summarized in the following and a $T$-$s$ diagram of the ideal process with heat regeneration is in Figure 18.5:

1. (1–2): Heat addition with a constant magnetic field, $H_0^{(1)}$
2. (2–3): Isothermal heat rejection to working fluid
3. (3–4): Heat rejection with a constant magnetic field, $H_0^{(3)}$
4. (4–1): Isothermal heat addition from working fluid

![Figure 18.5](https://example.com/figure18_5.png)

**FIGURE 18.5**
The magnetic work in the cycle is again equal to the confined area (1–2–3–4). The area (b–d–2–1) represents the regeneration heat that must be absorbed by the magnetocaloric material. In the ideal case, this area is equal to the heat rejected by the material (a–c–3–4). Since heat transfer is an irreversible process, however, this regeneration of the magnetic material reduces the overall efficiency of the cycles. The area (1–4–a–b) represents the cooling capacity of the Ericsson cycle.

The Ericsson and Stirling cycles are similar; the temperature span is greater than the Carnot cycle and, in the case of ideal regeneration, the Ericsson and Stirling cycles have a COP equivalent to that of the Carnot cycle. An important point to note for all of the cycles discussed so far is that all of the working material follows the same cycle. This is a subtle point but is important in understanding the AMR cycle that follows.

In theory, regeneration can provide high efficiencies and increased temperature spans; however, implementing this with magnetic refrigerants is not easy. Because the working substance is a solid, it is difficult to effectively couple the body to an external thermal storage medium that maintains a temperature distribution between the hot and cold reservoirs. Even if this can be solved, the refrigerants themselves have nonideal properties such that different amounts of heat need to be regenerated between the cooling and warming phases. These considerations were part of the reasoning that lead to the AMR cycle whereby the refrigerant itself is a regenerator linked to hot and cold reservoirs by a heat transfer fluid.

### 18.2.2.4 Active Magnetic Regenerator Cycle

The process currently employed in magnetic refrigeration cycles above 20 K is the AMR. The Brayton, Ericsson, and Stirling cycles all require high-quality regeneration to be efficient enough for magnetic refrigeration units to be competitive compared to vapor-compression units. The AMR cycle provides this by using the magnetic material itself as a regenerator that is in direct contact with the heat transfer fluid. Passive regenerators are used in various devices to increase the operating span. By using the working material itself as the thermal storage medium, the regenerator is said to be active [22]. A stepwise representation of the AMR process is shown in Figure 18.6. A schematic indicating the cycle-average temperature distribution and heat and work interactions at a location in the regenerator is shown in Figure 18.7.

The cycle is assumed to be in periodic steady state so that the temperature distribution is a stationary periodic function in time. The refrigerant is made to be a porous solid with a large surface area per unit volume. A heat transfer fluid flows in the pores, oscillating between the cold and hot reservoirs in synchronization with the magnetic field waveform. The steps begin with the regenerator being magnetized so that the local temperature of the solid increases due to the local MCE. Fluid is then blown from the cold side to the hot side absorbing energy from the matrix and exiting at a temperature above that of the warm reservoir. As a result, heat is rejected in the warm heat exchanger. The fluid flow stops, the magnetic field is removed, and the temperature decreases at all points due to the MCE. The temperature of solid material at the cold end is now less than it was when the cycle began. Fluid now flows through the bed in the opposite direction, exiting at a lower temperature such that heat will be absorbed from the cold reservoir. The fluid flow stops, the bed is remagnetized, and the cycle begins again.

The solid refrigerant acts as a regenerator to the heat transfer fluid. At one point in the cycle, the regenerator removes heat from the fluid, while at a later point, this heat is returned and an additional amount of energy is added due to magnetic work. This increases the fluid temperature exiting the hot end of the regenerator so that heat
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Can be rejected to the warm reservoir. The heat flux from the cold end to the warm end, \( Q \), varies with position in the regenerator. Integrated over the entire bed, the total work input will balance the net heat transfer. An AMR can use a single material as the regenerator or a combination of different materials. Using multiple materials complicates the regenerator design process but allows for a larger temperature span to be created between the hot and cold reservoirs.

Determining the optimal composition, structure, matrix geometry, and operating conditions of an AMR is an active area of research. The highly nonlinear properties of

FIGURE 18.6
A stepwise representation of an AMR cycle. (a) Magnetization, (b) magnetized fluid flow from the cold side to the hot side, (c) demagnetization, and (d) fluid flow from the hot to cold side. (From Pecharsky, V.K. and Gschnieder, K.A., Jr., *J. Magn. Magn. Mater.*, 200, 44, 1999. With permission.)
both first- and second-order materials make this a complex problem. Simplified analyses provide some guidance regarding the ideal MCE and flow conditions that satisfy the macroscopic entropy balance on a regenerator [48,49]. When the field-dependent specific heat of a refrigerant is taken into consideration, the ideal MCE as a function of temperature, $\Delta T(T)_{\text{ideal}}$, is given by

$$
\Delta T(T)_{\text{ideal}} = (\Delta T_{\text{ref}} + T_{\text{ref}}) \left( \frac{T}{T_{\text{ref}}} \right)^\sigma - T,
$$

(18.13)

where $\sigma$ is the ratio of specific heat at low field to that at high field and the subscript ref indicates the MCE at a reference temperature, $T_{\text{ref}}$. For this equation to be valid, the fluid thermal capacity ratio must also equal the specific heat ratio [48].

Although the temperature span is increased significantly with an AMR cycle and multiple refrigerants, a single AMR stage may not be enough to operate between 20 and 300 K. A number of AMR units can be arranged together to span large temperature differences, to increase cooling power, or to better match cooling to the enthalpy change of a fluid like hydrogen. In a series configuration, the cold reservoir of a warmer stage is also the hot reservoir of a lower-temperature stage. In a parallel configuration, one AMR stage precools hydrogen going to another stage with both stages rejecting heat to the same reservoir [50]. Because each stage in an overall liquefaction system may have different cooling loads and operating temperatures, an assortment of magnetocaloric materials are required. This adds a degree of complexity in the optimization of an entire liquefaction unit, in addition to added capital costs for building several AMRs. Irreversibilities resulting from various effects can also compound making minimization of entropy generation and losses in magnetic refrigeration an important exercise [23].

### 18.2.3 Regenerator Design

Magnetic liquefaction of hydrogen, like any process, contains irreversibilities. These irreversibilities reduce the efficiency of converting magnetic work into refrigeration, making
the overall process require more energy. Sources of inefficiency include nonideal materials, imperfect heat transfer, flow losses, eddy currents, and parasitic heat leaks in the device and from the environment.

Assuming suitable magnetic refrigerants are used, magnetic refrigerators using the AMR cycle require effective heat transfer. Regenerative heat transfer between the solid matrix and the fluid is done through direct contact, while transfer to the external reservoirs is through heat exchangers. If a single AMR stage is operating over a large temperature span, the impacts of imperfect convective heat transfer in the regenerator can be significant. In theory, because the cooling power of a device can be increased with the cycle frequency, there is a need for larger convective transfer rates. Optimizing regenerator structure and operating parameters using entropy generation minimization has also been performed on AMRs [51,52].

Regenerative heat transfer also requires careful design of the regenerator matrix so that the characteristic dimension of the structure is sufficiently small to ensure the material is being fully utilized [53]. Transfer of energy from the regenerators depends upon the solid thermal conductivity and specific heat. Higher conductivities allow for faster energy transfer to the working fluid, which reduces the time for parasitic heat leaks. Thermal diffusivity in the solid is linked to the operating frequency of an AMR through the Fourier number [54]. This plays an important role in optimized designs as the cooling capacity and losses of a system depend upon operating frequency. As discussed by Zhang et al., an optimum frequency exists, which minimizes the overall exergy destruction [23].

Other losses that contribute to decreased efficiency are flow losses and eddy currents. For a regenerator to have good thermal effectiveness, a large wetted area per unit volume is desired; however, this can lead to larger pumping powers needed to oscillate fluid through the structure. This problem becomes more significant as operating frequency increases. Eddy currents arise in conductors subjected to time-varying magnetic fields and are dissipated as heat due to resistance in the material. This problem scales with the square of the rate of field change [55]. Careful design choices and the use of materials with low electrical conductivity can minimize this problem. In the case of regenerators, spherical particle beds are common for the matrix, and, because of small size and point contacts between the particles, eddy-current losses can be small for typical operating frequencies [56].

18.3 Magnetocaloric Materials

Materials exhibit the MCE to varying degrees and single materials are only effective within a limited temperature range. This is one of the main challenges to developing commercial magnetic devices. A material with a wide operating range and a large MCE should reduce the required magnetic field strength while maintaining efficiency. This can benefit cost and relax some of the design constraints. For these reasons, developing and characterizing magnetocaloric materials is an integral part of improving magnetic refrigeration and facilitating the use of magnetic cycles for hydrogen liquefaction [57]. This section briefly discusses refrigerants, desirable properties, and materials relevant to hydrogen liquefaction and their operating range. This overview will be brief as the subject of materials is vast; the reader is encouraged to explore the literature for more details.
18.3.1 Requirements for an Effective Refrigerant

The choice of materials to use within a given cycle is still open to debate. In recent years, first-order materials have received a significant amount of attention due to large magnetic entropy changes using materials that are less expensive than rare-earth elements and intermetallic compounds on the basis of equivalent volume. Hysteresis tends to be significant in many of these materials and the width of the ordering transition in terms of temperature can be narrow.

18.3.1.1 Refrigerant Capacity

There are many properties that can be used to characterize refrigerants. Manufacturability, cost of materials and processing, toxicity, ductility, and a range of thermal properties can be considered. The most important are those that determine the ability to produce useful cooling efficiently; if this cannot be substantiated, the remaining properties are irrelevant. In terms of the AMR cycle, the ideal scaling of adiabatic temperature change with temperature has already been discussed. A general parameter used to characterize any refrigerant absorbing and rejecting heat isothermally is the refrigerant capacity (RC) as defined by Wood and Potter [57],

\[
RC \equiv \Delta S \Delta T_{sp},
\]

where, in a reversible cycle, the isothermal entropy change, \( \Delta S \), is the same for hot and cold heat transfer processes and \( \Delta T_{sp} \) is the temperature span. For a magnetic refrigerant, the magnetic entropy change as a function of temperature determines the maximum span and feasible operating points. For any magnetic refrigerant and applied field, a maximum value of RC can be determined. This parameter is useful in comparing magnetocaloric materials as it relates useful cooling to field strength on a volumetric basis. All other properties being the same, a material with a broad transition and large entropy change will have better potential as a refrigerant than one with a narrow transition and small entropy change.

A modified version of RC is used by Gschneidner and Pecharsky to compare materials [58]. They define a relative cooling power (RCP) in terms of the magnetic entropy change (RCP(S)) or the adiabatic temperature change (RCP(T)). The method is similar to [57]; however, to simplify things, they use the temperature span defined by the respective curve (entropy change or adiabatic temperature change) at half the maximum value, \( \delta T_{FWHM} \). The RCP values are normalized by the applied field strength so that RCP(S) has units of energy per unit volume of refrigerant per unit field, that is, J/cm\(^3\)/T. A subset of materials for use in the 20–80 K range are listed in Table 18.1 [58].

One interesting fact to note in Table 18.1 is the magnitude of the adiabatic temperature change per unit field change. These values are on the order of 1 K/T and are the primary reason why a pure magnetic stage for hydrogen liquefaction requires superconducting magnets and highly effective regenerator designs.

The shapes of magnetic entropy curves as a function of temperature for various materials active below 100 K are shown in Figure 18.8. As can be seen, there tends to be a trade-off between the maximum entropy change and the width of the transition. While some materials have larger entropy spikes, they are only effective within a short temperature range. For example, ErCo\(_2\) produces a large entropy spike around 35 K but becomes ineffective within 5 K in either direction, while GdNi\(_2\) has a lower maximum entropy change but is effective
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over a wide temperature span. Based on the RCP(S) values listed in Table 18.1, GdNi₂ has a better potential as a refrigerant. The use of GdNi and GdNi₂ in the AMR cycle operating between 20 and 80 K for hydrogen liquefaction was discussed by Zimm et al. [17].

As discussed previously with the AMR concept, one way to utilize materials with larger spikes, but narrow transitions, is to use regenerators that contain multiple materials. This allows for the overall entropy change to remain relatively constant over a broad temperature span. However, regenerators composed of more than one material become difficult to model theoretically and numerically. With this in mind, several test devices and models have been developed with the intent of testing and understanding the properties of AMRs specifically in the 80–20 K range [22, 24, 26, 27, 31, 33–36, 60].

### 18.3.1.2 Tailoring Properties

Another useful property for a magnetic refrigerant is the ability for its Curie temperature to be shifted by altering its composition. This allows a material to be used in a specific temperature range that may lack quality refrigerants or ones that are easy to work with. Furthermore, a less expensive material might be able to replace the operating region of a more expensive refrigerant.

#### TABLE 18.1

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ or $T_{max}$</th>
<th>$-\frac{\Delta S}{\Delta H}$ (mJ cm$^{-3}$ K$^{-1}$T)</th>
<th>$-\frac{\text{RCP(S)}}{\Delta H}$ (mJ cm$^{-3}$ T)</th>
<th>$\Delta H(T)$</th>
<th>$\Delta T_{ad}$ (K)</th>
<th>RCP(T) (K$^2$ T$^{-1}$)</th>
<th>$\Delta H(T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dy$<em>{0.05}$Er$</em>{0.15}$)Al$_2$</td>
<td>55.7</td>
<td>22.9</td>
<td>963</td>
<td>5</td>
<td>1.15</td>
<td>74.8</td>
<td>10</td>
</tr>
<tr>
<td>DyAl$_2$</td>
<td>63.9</td>
<td>22.0</td>
<td>951</td>
<td>5</td>
<td>1.10</td>
<td>73.7</td>
<td>10</td>
</tr>
<tr>
<td>GdNi$_2$</td>
<td>72</td>
<td>19.6</td>
<td>861</td>
<td>7</td>
<td>1.06</td>
<td>46.8</td>
<td>7</td>
</tr>
<tr>
<td>GdNi</td>
<td>72</td>
<td>—</td>
<td>—</td>
<td>7</td>
<td>0.85</td>
<td>40.1</td>
<td>7</td>
</tr>
<tr>
<td>HoCo$_2$</td>
<td>82</td>
<td>32.0</td>
<td>831</td>
<td>7</td>
<td>0.74</td>
<td>71.4</td>
<td>9</td>
</tr>
<tr>
<td>GdNiIn</td>
<td>94</td>
<td>13.9</td>
<td>1180</td>
<td>9</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

An example of a tunable alloy is Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$—the ordering temperature increases with Si content. The $x = 0.0825$ composition is shown in Figure 18.8. (Note: the label in the legend is missing the subscript 4.) Matsumoto et al. characterized the magnetization and entropy change of this alloy with a range of compositions specifically for use in hydrogen liquefaction [61]. While large entropy changes were measured, they also noted hysteresis, which is an irreversibility that may have a significant impact on performance. Rare-earth alloys such as Gd$_x$Er$_{1-x}$ are also tunable while maintaining good magnetocaloric properties.

One other avenue for creating a regenerator with desired properties is to produce a composite material that is a mixture of refrigerants [62–64]. This has been examined experimentally and theoretically for low- and high-temperature AMRs. One study of particular relevance for hydrogen liquefaction involved the creation of a composite material with a relatively uniform and broad magnetic entropy change below 80 K [63]. Creating a composite may create a better magnetic entropy curve; however, it will also create irreversibility due to heat transfer between particles.

### 18.3.2 AMR Performance

The consequences of material properties, regenerator composition, and operating parameters are discussed in a paper by Matsumoto et al. where an AMR hydrogen liquefaction unit operating from 77 to 20 K is analyzed numerically [26]. In the case of a single material AMR, the impacts of the working fluid's mass flow on the cooling capacity of the refrigerator are determined. It is found that both low and high mass flows reduce the cooling capacity while an intermediate value provides an optimum cooling capacity. The effect of using materials with different Curie temperatures is also assessed while maintaining the hot reservoir at 77 K and varying the overall temperature span of the bed. For materials with Curie temperatures of 60 K (Tc60), 70 K (Tc70), and 80 K (Tc80), each material appears beneficial in a different aspect. The Tc80 material provides the highest COP value, the Tc70 material provides the highest cooling capacity, and the Tc60 material has the smallest COP and cooling capacity.
Evaluating the results for the high cooling capacity of Tc70 reveals that this material exhibits the largest average entropy change within the 60–77 K region, which is similar to the operating temperature region. From this, it is deduced that the highest cooling capacity comes when a material provides the largest average entropy change within the operating region of the AMR. Therefore, although the Tc60 had the largest peak entropy change, its entropy change throughout the entire operating temperature range of the material bed was poor compared to the Tc70 material. This is consistent with the RC method of ranking materials.

These results also support the idea that using multiple materials for the regenerator in the AMR could be more beneficial than one material. Since the temperature of the refrigerant bed is distributed as shown in Figure 18.7, using multiple materials allows for each material in the bed to operate closer to its Curie point and the maximum entropy change. Matsumoto et al. analyzed the effect of two-layered AMR beds with different quantities of the Tc60 and Tc80. It was found that the highest cooling capacity is obtained when the material bed is 30% Tc60. The COP however decreased with an increasing percentage of the lower Curie temperature material giving rise to the notion that the high-temperature side plays an important part in reducing the irreversibilities of the cycle [26].

### 18.3.3 Refrigerant Selection

A large number of materials have been discovered that are potentially useful as magnetic refrigerants. Table 18.2 shows a list of some magnetic refrigerants and their Curie

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
<th>Material</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdMn$_2$</td>
<td>300</td>
<td>[65]</td>
<td>Gd$<em>5$(Si$</em>{0.025}$Ge$_{0.975}$)</td>
<td>75</td>
<td>[66]</td>
</tr>
<tr>
<td>Gd</td>
<td>293</td>
<td>[66]</td>
<td>GdN</td>
<td>65</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.3}$Y$</em>{0.1}$</td>
<td>281</td>
<td>[65]</td>
<td>DyAl$_2$</td>
<td>63</td>
<td>[66]</td>
</tr>
<tr>
<td>GdZn</td>
<td>268</td>
<td>[65]</td>
<td>Gd$<em>{0.025}$Er$</em>{0.75}$</td>
<td>60</td>
<td>[67]</td>
</tr>
<tr>
<td>Gd$<em>{0.25}$Dy$</em>{0.07}$</td>
<td>266</td>
<td>[66]</td>
<td>Gd$_{2.5}$S$_4$</td>
<td>58</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.8}$Y$</em>{0.2}$</td>
<td>254</td>
<td>[65]</td>
<td>Gd$<em>{0.05}$In$</em>{0.3}$</td>
<td>57</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.36}$Dy$</em>{0.64}$</td>
<td>234</td>
<td>[66]</td>
<td>Gd$<em>{0.5}$Er$</em>{0.5}$Al$_2$</td>
<td>51</td>
<td>[67]</td>
</tr>
<tr>
<td>GdZn$<em>{0.85}$In$</em>{0.15}$</td>
<td>224</td>
<td>[65]</td>
<td>Gd$<em>{0.7}$Th$</em>{0.3}$Al$_2$</td>
<td>50</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.67}$Y$</em>{0.33}$</td>
<td>211</td>
<td>[65]</td>
<td>Dy$<em>{0.2}$Er$</em>{0.3}$Al$_2$</td>
<td>45</td>
<td>[66]</td>
</tr>
<tr>
<td>GdGa</td>
<td>200</td>
<td>[65]</td>
<td>Gd$_{2.3}$S$_4$</td>
<td>42</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.16}$Dy$</em>{0.02}$</td>
<td>195</td>
<td>[66]</td>
<td>Gd$<em>{0.13}$Er$</em>{0.865}$Al$_2$</td>
<td>40</td>
<td>[67]</td>
</tr>
<tr>
<td>Gd$<em>{0.3}$La$</em>{0.3}$</td>
<td>185</td>
<td>[65]</td>
<td>GdNi$_2$ (amorphous)</td>
<td>38</td>
<td>[65]</td>
</tr>
<tr>
<td>Dy</td>
<td>180</td>
<td>[66]</td>
<td>Dy$<em>{0.2}$Er$</em>{0.5}$Al$_2$</td>
<td>38</td>
<td>[66]</td>
</tr>
<tr>
<td>GdAl$_2$</td>
<td>153</td>
<td>[65]</td>
<td>Gd$<em>{0.1}$Er$</em>{0.9}$Al$_2$</td>
<td>33</td>
<td>[67]</td>
</tr>
<tr>
<td>Gd$<em>{0.9}$Au$</em>{0.1}$</td>
<td>150</td>
<td>[65]</td>
<td>GdNi$_5$</td>
<td>32</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$_5$</td>
<td>135</td>
<td>[66]</td>
<td>Gd$<em>{0.13}$Th$</em>{0.36}$Al$_2$</td>
<td>30</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.65}$Ni$</em>{0.32}$</td>
<td>125</td>
<td>[65]</td>
<td>Gd$_{2.5}$Si$_2$</td>
<td>28</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.25}$S$</em>{0.75}$Ge$_{0.75}$</td>
<td>120</td>
<td>[66]</td>
<td>Gd$<em>{0.05}$In$</em>{0.2}$</td>
<td>24</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.65}$In$</em>{0.3}$</td>
<td>111</td>
<td>[65]</td>
<td>Dy$<em>{0.25}$Er$</em>{0.75}$Al$_2$</td>
<td>24</td>
<td>[66]</td>
</tr>
<tr>
<td>Gd$<em>{0.5}$Ag$</em>{0.5}$</td>
<td>100</td>
<td>[65]</td>
<td>Gd$_{2.75}$Si$_2$</td>
<td>21</td>
<td>[65]</td>
</tr>
<tr>
<td>Gd$<em>{0.9}$Th$</em>{0.3}$Al$_2$</td>
<td>90</td>
<td>[65]</td>
<td>Gd$<em>{0.05}$Er$</em>{0.972}$Al$_2$</td>
<td>20</td>
<td>[67]</td>
</tr>
<tr>
<td>Gd$<em>{0.25}$S$</em>{0.75}$Ge$_{0.75}$</td>
<td>90</td>
<td>[66]</td>
<td>ErAl$_2$</td>
<td>12</td>
<td>[66]</td>
</tr>
<tr>
<td>GdNi$_2$ (crystalline)</td>
<td>81</td>
<td>[65]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
temperatures. This list is not exhaustive but provides a good spread of materials from room temperature to the hydrogen boiling point.

Table 18.2 demonstrates the need for a wide range of refrigerants required to liquefy hydrogen from room temperature. Even if one material could be used for every 20 K temperature span, a minimum of 14 different materials would still be required. When considering the different combinations of materials that are possible, the design of a full magnetic liquefaction process from 300 K is complicated. Alternatively, hydrogen can be precooled by liquid natural gas (LNG) (112 K) or LN$_2$ (77 K) resulting in the use of fewer materials to reach liquid hydrogen. Given the challenge of a magnetic device operating between room temperature and liquid hydrogen, most designs have focused on a hybrid liquefier that used a conventional cycle to LN$_2$ and a magnetic stage(s) operating below 80 K. These low-temperature magnetic devices will be discussed in the following section.

### 18.4 20–80 K Magnetic Refrigeration Devices

A number of cryogenic devices have been developed to specifically test materials and operating parameters in the 80–20 K range. While not meant to be liquefiers, these devices were usually part of a liquefier development path, and results were used to assist in determining preferred configurations for magnetic stages operating below a LN$_2$ upper stage. Other devices have been developed to operate below 20 K using LH$_2$ as an upper heat sink or even below 4 K with LHe as the hot reservoir. Near-room-temperature MR is another active application area with device development activities. These devices will not be discussed further; instead, we will focus on those devices specifically relevant to LH$_2$ liquefaction. A discussion of some important design considerations for magnetic devices follows.

#### 18.4.1 Design Considerations

Some unique considerations arise when building devices utilizing magnetic fields. To maximize cooling power, magnetic fields are as high as practically possible. Constraints on this arise due to magnetic forces which, in some cases, also restrict operating frequency. Another consideration is sealing and one must decide if the regenerators are to have static or dynamic seals. Because superconducting magnets can be expensive, simple designs are preferred. The desire to use solenoid coils instead of complex windings leads to device geometries built around the magnet field shape and ability to access the high field region.

##### 18.4.1.1 Forces

Structural forces between current-carrying elements are present in systems using coil magnets (Lorentz forces); however, these are ignored as they typically concern the magnet design. The following discussion focuses on the forces related to magnetic work input.

A magnetic cycle requires cyclic application of a magnetic field waveform. This can be done in three ways: (1) fix a material and then charge and discharge a coil, (2) use a static field and move the AMR in or through the field, and (3) fix the AMR and move the field. The last two nearly are equivalent in theory, but differences arise due to the ability to create a semicontinuous regenerator structure and the appearance of a relatively constant permeability in the field region. Charging a coil is undesirable because of frequency
limitations and the additional power flows required due to the changing energy in the field. Some common configurations used are reciprocating AMRs and rotating structures housing regenerator beds. An analysis of force modeling for these two types of geometries was reported by Barclay et al. [68]. It was found that reciprocating geometries using single high field regions resulted in large unbalanced magnetic forces. This leads to an increase in structural and drive system ratings for these geometries. In the case of a rotating wheel regenerator structure, although there is good force balancing due to relatively constant permeability in the field region, there is however a radial force that must be designed for. An analysis of dynamic forces on a reciprocating AMR device is reported in [69]. Part of this work examined the use of a passive energy storage mechanism to reduce the size of a drive motor by damping out the reversing, unbalanced forces on the moving AMR structure. While reductions in torque were possible, the frequency of the torque waveform doubled and dynamic tuning would be needed.

A magnetic material in a field gradient will also have a net force. Magnetocaloric materials are subjected to magnetic forces when they are moved from regions of low field to high field, and the force depends upon the state of the material and the field variation in space. Forces on a refrigerant below the Curie temperature are higher than those above the Curie temperature. Regenerator matrix structures are often particle beds but can take various shapes. The matrix elements will be subjected to magnetic body forces that vary with location in the matrix and time. This can also create shear stresses and cyclic loading. Assuming the refrigerant is not too brittle, one of the main concerns with a particle bed is the movement and migration of particles. It is important that the solid matrix maintain its structure so that preferential flow paths do not arise and that the property distribution through the bed is as intended. Monolithic structures have advantages, but they can be difficult to make with large specific surface areas. One idea for creating a single structural element using particles is to bond them together [70]. This idea has been experimentally tested and does seem to work; however, because of the very small hydraulic diameters of the AMRs, creating the structure without affecting the homogenous nature of the void distribution is difficult. Another approach is to use sintered particle beds; however, maintaining material properties and eddy-current generation are concerns for this technique. Discrete microstructured elements can also be fabricated and used to create a larger regenerator and is a technique now being used.

18.4.1.2 Flow

The AMR concept requires effective regenerators in which the fluid–solid heat transfer occurs with small temperature differences. This must be balanced against pumping power requirements due to pressure drops through the regenerator and remaining fluid system. The regenerator is the element separating warm and cold temperature regions and must act as a thermal resistance between the reservoirs. These requirements come with trade-offs as good convective heat transfer often comes with small hydraulic diameters, which lead to higher pressure drops. No matter how oscillating flow is created and controlled, there will be a need for good sealing around the regenerator structure.

As with magnetic forces, the choices made in creating a magnetic field waveform for the refrigerant are linked to sealing requirements. Some designs can use static seals while others need dynamic seals. The latter are, of course, more challenging. Ideally, the void space in a regenerator is small and fluid flows uniformly through the matrix. Preferential channeling or leaks around the regenerator between the temperature reservoirs should be prevented. While rotating regenerator structures simplify the magnetic forces and
structural and drive system requirements, they usually have dynamic seals between the moving regenerators and the stationary housing. A good dynamic seal may impose additional losses due to friction. Dynamic seals must also be able to operate over long periods at cryogenic temperatures.

When using magnetic refrigeration stages for liquefaction, ideally, sensible heat is removed from hydrogen at a number of intermediate temperatures. However, sensible cooling can also occur using a portion of the cold AMR heat transfer fluid bypassing the regenerators and, instead, absorbing energy from the hydrogen stream through a heat exchanger [71]. Not only does this reduce entropy generation in cooling the hydrogen gas, it can also help to thermally balance the regenerator. This latter effect arises due to the difference in heat capacity of the refrigerant between high and low fields. As will be seen later, bypass flow configurations have been implemented in the design of staged magnetic liquefiers.

18.4.1.3 Parasitic Magnet Load

An unavoidable parasitic load for magnetic refrigeration systems using superconducting magnets arises from the need to maintain the magnet at operating temperature. The needed cooling power can be relatively small as magnets can be operated in persistent mode, which means the power supply for the field is no longer needed. The parasitic load is then dominated by heat leaks to the magnet. The impacts of magnet cooling have been studied and results show that the impact on efficiency depends upon the operating temperature of the magnetic refrigerator and the cooling power of the device [72]. For low temperatures and high cooling powers relative to the magnet cooling requirement—as with hydrogen liquefaction applications—the impact of magnet cooling requirements can be very small. This study is now somewhat dated and had assumed a superconducting magnet operating at 4.2 K. Given recent progress using high-temperature superconductors to build magnets, the impacts of magnet parasitic load may be even less of a concern, particularly for hydrogen liquefaction.

18.4.2 Cryogenic AMR Devices

Although designs for AMR devices for hydrogen liquefaction include reciprocating and rotary configurations, to date, all experimental devices operating between 80 and 20 K have been reciprocating. Experimental and theoretical results for some of these devices will be discussed.

The development of a test device designed to study magnetic refrigeration between 77 and 20 K using a lead recuperator was discussed by Matsumoto et al. [33]. This device did not use the refrigerant itself as a regenerator and, unlike the AMR cycle, the entire mass of refrigerant underwent the same cycle. This piston-type reciprocating device used sintered DyAl$_{2.2}$ as a refrigerant. In the design, the regenerator was moved by a piston throughout the cycle, transferring heat to and from the magnetic material. The refrigeration unit was found to produce a temperature span of between 50.3 and 58.7 K in the regenerator and 48.3 and 59.1 K in the magnetic refrigerant for a 5 T magnetic field and a cycle of 300 s. The primary source of losses noted in the experiment were due to poor heat transfer between the two solid materials of the regenerator and the magnetic refrigerant.

Degregoria et al. [34] describe an AMR refrigeration apparatus, seen in Figure 18.9, using an immersion-cooled superconducting magnet with fields up to 7 T. A novel feature of this design is that the magnet reciprocates while the regenerator beds are stationary. This allows for static sealing and simple flow system design.
AMR performance was investigated in the range of 10–20 K using Er\textsubscript{1−x}Gd\textsubscript{x}Al\textsubscript{2} and in GdNi\textsubscript{2} in the 40–80 K range. Tests were performed using fields of 5 and 7 T and results were compared to numerical predictions. The regenerator matrix was crushed irregular particles. Numerical results overestimated the actual test data; however, a zero-load temperature span of \(\sim 44\) K was achieved at 5 T using GdNi\textsubscript{2}. Errors in the model predictions were suggested to be a combination of poor correlations and uncertain material properties.

Wang et al. [35] describe experimental results using an AMR test apparatus described in [34] but modified to use a LN\textsubscript{2} heat sink (seen in Figure 18.10) instead of a separate cryocooler. This modification allowed the heat rejection to be quantified by monitoring the boil-off rate. Heat loads could be set using a resistive heater in the cold section.

A large number of tests were performed using GdNi\textsubscript{2} with a focus on efficiency measures of the intrinsic AMR cycle, that is, using the magnetic work and pumping work across the regenerators. The sensitivity of efficiency to fluid displaced through the regenerator, temperature span, and cooling load was also measured. The intrinsic efficiency was found to be higher than 50% of Carnot over a range of operating conditions. This work suggests that with appropriate materials, the AMR cycle can produce high efficiency.

Zimm et al. [36] describe a reciprocating test apparatus using a stationary, 7 T superconducting magnet. One of the goals of this device shown in Figure 18.11 was to increase the amount of refrigerant significantly from previous tests and maximize the use of the high field volume. A total of four kilograms of GdNi\textsubscript{2} was used in the tests. The use of flex hoses to couple the reciprocating regenerator assembly to the heat exchangers resulted in a

\[\text{Rejected heat} = \dot{Q}_{\text{hot, total}}\]

\[\dot{W} = \dot{Q}_{\text{hot}} - \dot{Q}_{\text{cold}}\]
significant dead volume in the flow circuit. Numerical predictions suggested that a much larger cooling power could be obtained than was experimentally achieved and the flex hose volume was identified as a serious problem. Inserting Teflon liners to reduce the dead volume nearly doubled the cooling power.

Another reciprocating test apparatus was created by Rowe et al. with the intent of testing different regenerator materials and configurations with little turnover time [27]. This unit has the ability to test refrigerants over a wide range of temperatures to determine their effectiveness and temperature spans in relation to different magnetic fields. Various refrigerant geometries can be used in single or multimaterial regenerator beds. The device uses small quantities of materials, which reduces material costs and design forces and can operate at frequencies as high as 1 Hz. Figure 18.12 shows a schematic of the apparatus configured for operation with LN₂.

Unlike the previous devices, this apparatus was designed to allow testing from room temperature down to 20 K. Most of the reported results using the device are for
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Magnetic liquefaction of hydrogen near-room-temperature operation; however, tests have been carried out using GdNi$_2$, DyAl$_2$, and Gd$_5$Si$_{0.33}$Ge$_{3.67}$ alone and in layered structures. Results using Gd$_5$Si$_{0.33}$Ge$_{3.67}$ were reported in [23]. Due to an inability to maintain the hot heat sink much below 90 K, the maximum no-load span was 8 K at 5 T. Thus, the operating point was far above the temperature of the peak MCE (~75 K). Near-room-temperature tests using a three-material regenerator and 5 T produced a peak no-load temperature span of ~85 K.

Experience gained with test devices as well as model results has been used to guide the design of magnetic liquefiers of hydrogen. A limited amount of work on magnetic liquefaction is currently being performed in Japan, the United States, and Canada. Some liquefier concepts will be discussed in the following section.

18.5 Magnetic Liquefier Concepts

A wide variety of research has occurred in the field of magnetic refrigeration to determine preferred system configurations for hydrogen liquefation. Although the AMR cycle is at the heart of system designs, many process configurations are still being assessed.
These include the number of AMR stages, how they are cascaded together, the type and number of materials to use, and the best operating parameters. Some processes utilize only magnetic cycles to span the 300–20 K temperature gap, while others use LN$_2$ or LNG to precool hydrogen before being liquefied magnetically. These are areas being investigated to improve the overall efficiency and cost-effectiveness of magnetic hydrogen liquefaction units.

18.5.1 Process Configurations

This section describes process flow configurations proposed for liquefying hydrogen with magnetic cycles. Recently, three different configurations have been analyzed by Utaki et al. [25] using the numerical model by Engelbrecht [73]. All three cases use series cascades of AMR systems with different precooling temperatures. Each configuration uses a magnetic Carnot stage (CMR) for the final removal of latent heat and liquefaction [20]. It is difficult to ascertain, but it appears that bypass flow is assumed in some stages. This study also looks at using hydrogen, propane, and glycol/water mixture as heat transfer fluids.

The starting temperatures for the three cases are 300, 77, and 120 K. Starting points of 77 and 120 K are established by precooling hydrogen with LN$_2$ and LNG, respectively. The model results for all cases assume a constant magnetic entropy change of 86.2 mJ/cm$^3$ K at 5 T independent of temperature. This assumes an ideal magnetocaloric material in an ideally layered regenerator. Making this assumption removes the dependency on available materials, allowing for a comparison between the fundamental configurations of each of the three cases. The heat emitted by the conversion from ortho-hydrogen to para-hydrogen
Magnetic Liquefaction of Hydrogen

is also taken into account in the model and is included as a heat load during each of the liquefaction processes. To compare the work, COP, and liquefaction efficiencies, all cases produce the same amount of hydrogen and use optimized regenerator beds and mass flows for each stage.

The first case shown in Figure 18.13 utilizes seven AMR stages from room temperature to 22 K where a CMR stage is used to liquefy hydrogen from 22 to 20 K. The working fluids for the AMR stages are a 56% ethylene glycol/water mix from 300 to 235 K, liquid propane from 235 to 95 K, and gaseous hydrogen from 95 to 22 K. Ethylene glycol/water and liquid propane are used as these fluids were found to have a significantly higher COP per stage. The use of hydrogen as the heat transfer fluid in an AMR offers some potential advantages over helium; however, the ability of known refrigerants to operate in an H\textsubscript{2} environment is unknown.

The second case uses LN\textsubscript{2} to precool hydrogen to 77 K. From this point, hydrogen is cooled to 22 K through three AMR stages and then liquefied using a CMR. In the final case, gaseous hydrogen is first cooled to 120 K by LNG and then run through five AMR stages and a CMR liquefaction stage. Both cases 2 and 3 use hydrogen as the working fluid in the system. Process flow diagrams for cases 2 and 3 are provided in Figure 18.14.

Since the appeal of magnetic refrigeration is its theoretically low energy cost compared to gas systems, the most important results from the three separate cases are the work input and liquefaction efficiency. The work input is described as the work required to liquefy hydrogen from room temperature. In the case where precooling is performed with LN\textsubscript{2}, additional energy is added to the AMR and CMR work totals to account for the work input to the nitrogen liquefier. The efficiency of each process is found by dividing the theoretical liquefaction energy by the actual energy required. For liquid hydrogen, which has been converted to ortho–para equilibrium, this theoretical work is 3.92 kWh/kg H\textsubscript{2} [39]. In the paper by Utaki et al., a 0.01 ton H\textsubscript{2}/day unit is modeled so the minimum power required is then 1.63 kW. All three units are assumed to produce the same amount of product, making the CMR work identical in all cases. A Carnot efficiency of 50% is assumed based upon previous tests, making the power required for the CMR stage 1.30 kW [21]. Table 18.3 summarizes the work requirements for each part of the three cases in addition to the liquefaction efficiency of hydrogen.

From Table 18.3, case 2 shows the highest liquefaction efficiency at 46.5% followed closely by case 3 at 46.3%. Factors to take into account include the added capital cost for the additional AMR units in the 5-stage process and increased irreversibilities that may occur in using a larger number of stages. Another result to note is the decreased amount of work in case 1 when the number of AMR stages is increased from seven to nine. The added stages allow for each AMR to cover smaller temperature spans resulting in an overall more efficient system.
Other process configurations using series and parallel AMR stages have been identified for efficient hydrogen liquefaction [50]. While multistaged processes can reduce operating costs by better matching the cooling requirements of hydrogen, capital costs may ultimately limit the number of stages. Some of the more detailed magnetic liquefier designs reported in the literature are discussed in the next section.

### 18.5.2 Liquefier Designs

To date, a small number of magnetic liquefier designs have been developed and analyzed in detail. These devices are summarized here and provide a background for the current development activities on magnetic liquefaction discussed in the final section.

#### FIGURE 18.14

Case 2 (a) contains 3 AMR stages with a CMR stage and case 3 (b) contains 5 AMR stages with a CMR stage. (From Utaki, T. et al., *Cryocooler*, 14, 645, 2007.)

#### TABLE 18.3

Summary of the Input Work and Liquefaction Efficiency for Cases 1–3

<table>
<thead>
<tr>
<th>Case 1 (7 Stages)</th>
<th>Case 1 (8 Stages)</th>
<th>Case 1 (9 Stages)</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precooling work (kW)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.49</td>
</tr>
<tr>
<td>AMR work (kW)</td>
<td>13.09</td>
<td>11.08</td>
<td>9.90</td>
<td>0.72</td>
</tr>
<tr>
<td>CMR work (kW)</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>Total work (kW)</td>
<td>14.39</td>
<td>12.38</td>
<td>11.20</td>
<td>3.51</td>
</tr>
<tr>
<td>Liquefaction efficiency (%)</td>
<td>11.4</td>
<td>13.2</td>
<td>14.6</td>
<td>46.5</td>
</tr>
</tbody>
</table>

An early design operating with a LN\textsubscript{2} precooling system was analyzed by Zhang et al. \cite{23,74}. The device depicted in Figure 18.15 uses three magnetic stages in series with ortho–para conversion assumed as a load for each stage. In the analysis, the cooling power and exergetic equivalent losses of the process are examined by altering various system parameters including material type, bed size, and temperature. Each regenerator stage in the design is also assumed to be made of a mixture of alloys from the family Gd\textsubscript{1−x}Er\textsubscript{x}Al\textsubscript{2}, while the heat transfer fluid in the AMR system is helium at 10 atm. This fluid is then used to cool a 1 atm hydrogen stream through external heat exchangers. Entropy generation and exergy balances are used to determine the impacts of inefficiencies in the regenerators, auxiliary refrigeration units, and external heat exchangers.

**FIGURE 18.15**
The aforementioned configuration represents the three-stage AMR liquefier used in the exergy analysis. (From Zhang, L. et al., *Cryogenics*, 33, 667, 1993.)
Several design features were suggested from the study to improve the efficiency of liquid hydrogen production using this specific configuration and operating space. The first suggestion is to use a large magnetic material bed. A larger material bed reduces the exergy losses relative to the cooling capacity produced. The material bed should also be a shape that maximizes heat transfer to the working fluid. Increasing the mass flow of the helium was identified as a way of reducing losses by decreasing the temperature difference between the working fluid and the stage temperature. This causes the cooling capacity to increase while the exergy destruction remains relatively constant. Alternately, the cycle’s frequency can also be increased to achieve the same effect. A novel finding from this research is that using a high magnetic field may not always be advantageous to the overall system.

Following the test results for the AMR reported by Degregoria and described earlier [34], Janda et al. designed a process to liquefy hydrogen at a rate 0.01 ton H$_2$/day with the intention to eventually scale this up to 1 ton/day. The device uses two stages to span from 80 to 20 K and is shown in a simplified form in Figure 18.16. Helium is used as the working fluid in the AMRR while precooling is again performed using LN$_2$. The previously tested material GdNi$_2$ is hypothesized to span from 80 to 40 K under a 7 T magnetic field, while GdPd was to be used in the 40 to 20 K stage with a 5 T field. Although this specific unit was never built, it provided a foundation for a number of studies [18,19,23,74]. The most recent activity related to this device was an optimization study by Zhang et al. [19], which studied the impacts of particle size, material bed lengths, and the interstage temperature on the overall process efficiency.

A novel feature of the design is the use of unbalanced flow in the regenerators. This may actually benefit the AMR cycle efficiency due to the variation in specific heat of the magnetic material. If the materials are largely operating below their Curie temperatures,
the specific heat in the demagnetized state is larger than when magnetized. For a local Brayton-type process to occur with this varying specific heat, the thermal mass of fluid should be different for high and low field blows. The optimized results indicated that the bypass ratio for the low-temperature stage was on the order of 12%, whereas for the high-temperature stage, it was \(\sim 2.5\%\). The optimal interstage temperature of the process was found to be 41 K, and the liquefaction efficiency was determined to be \(\sim 20\%\). This is a good number given the scale of the device.

As part of the Japanese World Energy Network project phase II, the potential of magnetic refrigeration for large-scale liquefaction at high efficiencies was investigated [66]. This study began by analyzing a 10 kg/day laboratory prototype. The schematic of the device is shown in Figure 18.17. One of the main design features is the use of a belt carrying discrete regenerator beds. The reason for this is so that an inexpensive solenoidal superconducting magnet could be used. The belt rotates the regenerators through the high and low field regions where manifolds are used to regenerate pressurized helium flowing through the heat exchange system. This type of design has the benefits of a rotary configuration in terms of force balancing; however, sealing and controlling flow is not a trivial problem. The design calculations assumed operation between room temperature and 20 K with six stages in parallel and the need for 14 different magnetocaloric materials. Overall, liquefaction efficiency was estimated to be \(\sim 50\%\).

Currently, research and development activities are occurring in Japan, Canada, and the United States. The US DOE is funding the development of a magnetic liquefier prototype by Heracles Energy [75]. In Canada, magnetic liquefaction is being studied by our group as part of a strategic research network on hydrogen (H2Can) funded by the Natural Sciences and Engineering Research Council of Canada (NSERC).

In Japan, recent work on hydrogen liquefaction was reported by Matsumoto et al. [21]. Their design is based upon the AMRR system of Utaki (discussed earlier) where hydrogen is precooled by LNG then run through three AMR stages and a final CMR liquefaction stage.

**FIGURE 18.17**
Schematic of an AMRR device using a belt of regenerators as the magnetocaloric material. (From Iwasaki, W., *J. Hydrogen Energy*, 28, 559, 2003. With permission.)
The starting point of 112 K was chosen due to the abundance of LNG plants in Japan. Because the AMR stages of this device have already been described, this final section will focus on the CMR stage.

The CMR converts gaseous hydrogen at 22 K to liquid hydrogen at 20 K. This is done through condensing hydrogen directly onto the refrigerant itself. Because most refrigerants are not hydrogen resistant, a ceramic material is used for this stage. This CMR refrigerant is Dy$_{2.4}$Gd$_{0.6}$Al$_{5}$O$_{12}$, or DGAG, and the thermal efficiency as compared to the ideal Carnot cycle is between 50% and 60% and the liquefaction efficiency is ∼90% [21]. The active magnetic refrigerator stages have not yet been fixed in terms of the number of stages and materials used, but the entire process is to be examined in the near future from either a LN$_2$ or LNG starting point. A cross-sectional view of the test apparatus and CMR and AMR stages are seen in Figure 18.18.

18.6 Summary

When Brown used gadolinium as a magnetic refrigerant in 1976, the seed for magnetic liquefaction of hydrogen was planted. Thirty-five years later, a broad array of research has been performed, improving our understanding of magnetocaloric materials, regenerator design, magnetic devices, and liquefaction processes. Studies addressing design principles, test devices, and magnetic refrigerants have proven that high efficiencies are possible; however, the development of commercial devices is still a challenge. The AMR cycle is the preferred method of generating cooling over significant temperature spans, but the thermodynamic implications of using multiple materials in a single AMR are still
being developed. Highly nonlinear material properties and a lack of analytic expressions describing AMR behavior make design a challenge. Devices operating with high magnetic fields must also accommodate for magnetic forces. Depending upon the chosen device geometry, these forces can be high and reversing and may lead to eddy-current heating and other losses. While numerous magnetic refrigerants have been identified, there appears to be a trade-off between the maximum MCE and the width of the magnetic transition. Layered AMR geometries may partially solve this problem, but there are limited experimental results to date.

With all of those mentioned earlier in mind, it should also be pointed out that the cumulative amount of work on magnetic liquefier development is relatively small compared to the effort that has gone into gas cycles. Gas compression and expansion technologies are mature with a diverse set of component manufacturers serving the market. As a result, we are likely to see only modest gains in conventional liquefier efficiency. The capital costs of large-scale conventional systems could easily decrease if repeated builds of standardized designs were to occur. Magnetic refrigeration provides an alternative process that may reduce the costs of liquid hydrogen at device scales that are uneconomical with conventional cycles. Higher efficiencies at smaller scales would allow liquefaction systems to be deployed in a more distributed manner instead of at large central facilities as we currently see. The preferred geometries and process configurations of magnetic liquefaction systems are still unknown, but with continued advances in high-temperature superconductors, materials, and our understanding of magnetic cycles, the prospects for commercialization of magnetic liquefiers are improving.

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