Impact of hysteresis on caloric cooling performance

Masche, Marvin; Ianniciello, Lucia; Tušek, J.; Engelbrecht, Kurt

Published in:
International Journal of Refrigeration

Link to article, DOI:
10.1016/j.ijrefrig.2020.10.012

Publication date:
2021

Document Version
Peer reviewed version

Citation (APA):
Highlights

- 1D regenerator model with hysteresis is used to assess caloric cooler’s performance
- Modeling of six hypothetical materials with different caloric properties
- Effect of hysteresis is greater on coefficient of performance than on cooling power
- Materials with low isothermal entropy change are very sensitive to hysteresis
- Materials with low specific heat can tolerate high hysteresis values
Impact of hysteresis on caloric cooling performance

M. Masche,1 L. Ianniciello,1,*) J. Tušek,2 K. Engelbrecht1

1Department of Energy Conversion and Storage
Technical University of Denmark – DTU
Anker Engelunds Vej B301,
2800 Kgs. Lyngby, Denmark

2Faculty of Mechanical Engineering
University of Ljubljana
Aškerčeva cesta 6,
SI-1000 Ljubljana, Slovenia

(Dated: October 13, 2020)

E-mail: luciann@dtu.dk (L. Ianniciello)

Abstract

Caloric cooling relies on reversible temperature changes in solids driven by an externally applied field, such as a magnetic field, electric field, uniaxial stress or hydrostatic pressure. Materials exhibiting such a solid-state caloric effect may provide the basis for an alternative to conventional vapor compression technologies. First-order phase transition materials are promising caloric materials, as they yield large reported adiabatic temperature changes compared to second-order phase transition materials, but exhibit hysteresis behavior that leads to possible degradation in the cooling performance. This work quantifies numerically the impact of hysteresis on the performance of a cooling cycle using different modeled caloric materials and a regenerator with a fixed geometry. A previously developed 1D active regenerator model has been used with an additional hysteresis term to predict how modeled materials with a range of realistic hysteresis values affect the cooling performance. The performance is quantified in terms of cooling power, coefficient of performance (COP), and second-law efficiency for a range of operating conditions. The model shows that hysteresis reduces efficiency, with COP falling by up to 50% as the hysteresis entropy generation ($q_{hys}$) increases from 0.5% to 1%. At higher working frequencies, the cooling performance decreases further due to increased internal heating of the material. Regenerator beds using materials with lower specific heat and higher isothermal entropy change are less affected by hysteresis. Low specific heat materials show positive COP and cooling power up to 2% of $q_{hys}$ whereas high specific heat materials cannot tolerate more than 0.04% of $q_{hys}$.

Keywords: hysteresis; caloric effect; 1D model; solid state cooling; first order phase transition
Nomenclature

\[ A_c \]  \quad \text{cross-sectional area (m}^2\text{)}
\[ Nu \]  \quad \text{Nusselt number (-)}
\[ AMR \]  \quad \text{active magnetic regenerator}
\[ p \]  \quad \text{pressure (Pa)}
\[ a_s \]  \quad \text{specific area (m}^{-1}\text{)}
\[ P \]  \quad \text{polarization density (C} \cdot \text{m}^{-2}\text{)}
\[ B \]  \quad \text{magnetic flux density (T)}
\[ Pr \]  \quad \text{Prandtl number (-)}
\[ c \]  \quad \text{specific heat (J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}\text{)}
\[ q \]  \quad \text{specific heat generation (J} \cdot \text{kg}^{-1}\text{)}
\[ COP \]  \quad \text{coefficient of performance (-)}
\[ Q \]  \quad \text{heat generation (J)}
\[ D_h \]  \quad \text{hydraulic diameter (m)}
\[ Re \]  \quad \text{Reynolds number (-)}
\[ E \]  \quad \text{electric field strength (V} \cdot \text{m}^{-1}\text{)}
\[ s \]  \quad \text{specific entropy (J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}\text{)}
\[ F \]  \quad \text{applied field to generate caloric effect (-)}
\[ S \]  \quad \text{entropy (J} \cdot \text{K}^{-1}\text{)}
\[ FOPT \]  \quad \text{first-order phase transition}
\[ SOPT \]  \quad \text{second-order phase transition}
\[ H \]  \quad \text{magnetic field intensity (A} \cdot \text{m}^{-1}\text{)}
\[ T \]  \quad \text{temperature (K)}
\[ HFC \]  \quad \text{hydrofluorocarbon}
\[ U \]  \quad \text{internal energy (J)}
\[ HC \]  \quad \text{hydrocarbon}
\[ V \]  \quad \text{volume (m}^3\text{)}
\[ k \]  \quad \text{thermal conductivity (W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\text{)}
\[ M \]  \quad \text{magnetization (A} \cdot \text{m}^{-1}\text{)}
\[ W \]  \quad \text{input work (J)}
\[ m \]  \quad \text{mass (kg)}
\[ x \]  \quad \text{axial position (m)}
\[ m \]  \quad \text{mass flow rate (kg} \cdot \text{s}^{-1}\text{)}

Subscripts
\[ \text{ad} \]  \quad \text{adiabatic}
\[ \text{av} \]  \quad \text{average}
\[ \text{BC} \]  \quad \text{barocaloric}
\[ \text{C} \]  \quad \text{cold}
\[ \text{c} \]  \quad \text{cooling}
\[ \text{demag} \]  \quad \text{removal of magnetic field}
\[ \text{depol} \]  \quad \text{removal of polarization}
\[ \text{depress} \]  \quad \text{removal of pressure}
\[ \text{disp} \]  \quad \text{dispersion}
\[ \text{EC} \]  \quad \text{electrocaloric}
\[ \text{eC} \]  \quad \text{elastocaloric}
\[ \text{f} \]  \quad \text{fluid}
\[ \text{F} \]  \quad \text{applied field}
\[ \text{H} \]  \quad \text{hot}
\[ \text{hys} \]  \quad \text{hysteresis}
\[ \text{iso} \]  \quad \text{isothermal}
\[ \text{load} \]  \quad \text{application of strain}
\[ \text{mag} \]  \quad \text{application of magnetic field}
\[ \text{max} \]  \quad \text{maximum}
\[ \text{MC} \]  \quad \text{magnetocaloric}
\[ \text{pol} \]  \quad \text{application of polarization}
\[ \text{press} \]  \quad \text{pressurizing}
\[ \text{stat} \]  \quad \text{static}
\[ \text{unload} \]  \quad \text{removal of strain}

Greek letters
\[ \varepsilon \]  \quad \text{strain (\%)}
\[ \eta \]  \quad \text{dynamic viscosity (Pa} \cdot \text{s)}
\[ \eta_{II} \]  \quad \text{second-law efficiency (\%)}
\[ \phi \]  \quad \text{porosity (\%)}
\[ \mu \]  \quad \text{magnetic permeability (H} \cdot \text{m}^{-1}\text{)}
\[ \rho \]  \quad \text{density (kg} \cdot \text{m}^{-3}\text{)}
\[ \sigma \]  \quad \text{stress (MPa)}
\[ \tau_{\text{cycle}} \]  \quad \text{cycle time (s)}
1. INTRODUCTION

Research on alternative cooling techniques based on solid-state refrigerants, generally called caloric cooling, has received interest recently thanks to reports on attractive caloric properties that can be used for solid state cooling. Cycles built around the temperature increase/decrease of materials associated with the application/removal of an external field could have the potential to become a more efficient alternative to conventional vapor compression cooling technologies (Bansal et al., 2012; Qian et al., 2016b). Caloric cooling is also an environmentally friendly cooling technology, as it can operate without refrigerants, which can be hazardous (e.g., NH₃) greenhouse gases (e.g., HFCs) (Dincer, 2003), or flammable (e.g., HCs). Caloric properties exist for ferroic materials (i.e. the caloric materials) that exhibit a reversible temperature change, known as the caloric effect, when an external field is applied. Depending on the external field, the caloric effect is either magnetocaloric (magnetic field), electrocaloric (electric field), barocaloric (hydrostatic pressure) or elastocaloric (uniaxial stress). A review of magnetocaloric cooling is given by Kitanovski et al., (2015b), a review of electrocaloric cooling is given by Wang et al., (2018), an elastocaloric cooling summary is given by Qian et al., (2016a) and Kabirifar et al., (2019), and barocaloric cooling is discussed by De. Oliveira et al., (2014). Caloric effects are also interesting in materials that exhibit multiple-coupled ferroic properties. Those materials are called multiferroics and are discussed by Fähler et al., (2012). The coupling of caloric effects within the same material can improve the system performance.

The potential of each cooling technology is determined by the caloric properties that are available and the ease of applying the field to drive the caloric effect. Magnetocaloric cooling is the most mature technology with devices reported that can operate at or near commercially relevant cooling loads and temperature spans (Aprea et al., 2015; Eriksen et al., 2015; Govindappa et al., 2018; Jacobs et al., 2014; Jeong, 2014), while no working barocaloric devices have been presented to date (Kitanovski et al., 2015a). Research on electrocaloric devices is still in the proof-of-concept stage, but several small demonstrators have been reported (Cheng and Zhang, 2015; Greco et al., 2019; Gu et al., 2013; Ma et al., 2017; Plaznik et al., 2019). Elastocaloric cooling devices are at a similar level as electrocaloric devices, with a few demonstrators reported (Engelbrecht, 2019; Greco et al., 2019; Schmidt et al., 2015). Recent devices with increased performance have been reported by Snodgrass and Erickson, 2019 and Wang et al., 2019.

Caloric cooling is overall a relatively new research area, but several recent publications have highlighted the potential impact of the technology. In an assessment of potential energy
savings for alternatives to conventional vapor compression cooling, Goetzler et al., (2014) ranked elastocaloric cooling as the most promising alternative cooling technology and magnetocaloric cooling as the fourth most promising. Brown et al., (2012) analyzed five alternative cooling technologies and concluded that magnetocaloric cooling and thermoacoustic cooling have the best prospects followed by thermo-tunnel, thermoelectric, and thermionic cooling. Other caloric technologies were not considered in the study.

There is a broad range of caloric materials reported, both with first and second order phase transitions (Gottschall et al., 2019). The most widely studied caloric materials are still magnetocaloric materials, and a recent review can be found by Gottschall et al., (2019). A range of barocaloric materials has been reported with properties that are generally similar to magnetocaloric properties, but recently barocaloric materials with the largest reported caloric effects have been reported by Lloveras et al., (2019) and Li et al., (2019). Electrocaloric materials are an active research topic, and many reported materials have attractive caloric properties. A summary of electrocaloric materials reported is given by Scott, (2011) and (Shi et al., 2019). Elastocaloric materials have received large interest for their shape memory and superelastic properties (Tobushi et al., 1998), and recently, more attention has been paid to their elastocaloric properties (Bonnot et al., 2008). New caloric materials are continuously being produced and reported, but it is not straightforward to assess new materials due to the complex interplay between caloric properties and thermal, mechanical and electrical properties.

First-order phase transition (FOPT) materials that experience a discontinuous phase change associated with a caloric effect are very promising for caloric cooling. These materials generally have a high entropy change when a field is applied, but typically also experience a hysteresis effect. Fähler et al., (2012) stated that more than a high entropy change with applied field is needed to achieve a high cooling performance in a real device. This work addresses how the hysteresis in different caloric materials (with different specific heats and isothermal entropy changes) influence caloric cooling performance. The impact of the hysteresis losses on the performance of a caloric cooling device has not yet been addressed systematically, although it could have a major impact on performance. There are only a few works (Brey et al., 2014; Plaznik et al., 2019) addressing this issue, but they are focused on a single caloric material with fixed properties. Very recently, Hess et al., (2020) presented a new phenomenological model incorporating thermal hysteresis of caloric materials, based on which they studied the second-law efficiency of four different caloric materials in a Carnot-like thermodynamic cycle.

The modeling approach provides an efficient way to predict the performance of an active magnetic regenerator (AMR) cooling cycle. A number of papers devoted to modeling AMRs can be found in the literature. The 1D porous media approach has recently been shown to
give good agreement with experiments by Christiaanse et al., (2019); Mugica Guerrero et al., (2017); Park et al., (2015); Plaznik et al., (2013); Teyber et al., (2019); Vuarnoz and Kawanami, (2013); You et al., (2016); Kim and Jeong, (2011). Other groups have recently reported 2D (Aprea et al., 2018; Lionte et al., 2015; Aprea et al. 2015) and 3D (Mugica et al., 2018) AMR models, while semi-analytical approaches have also been shown to give good agreement with experimental AMR results (Burdyny et al., 2014). Trevizoli et al., (2016) showed that model predictions are in better agreement with experimental results when heat losses from the system are included. Because the focus of this paper is to study how material properties influence AMR performance generally, a 1D model that neglects thermal losses has been implemented. 1D models have been shown to capture an acceptable level of system detail while using considerably less computing power than 2D and 3D and are therefore a good choice for this study.

In this work rather than studying specific materials reported in the literature, the material properties are approached more generally by constructing representative materials with hypothetical caloric properties, inspired by existing materials, and a range of representative hysteresis values. The impact of hysteresis and specific heat is studied for six materials with different caloric properties that approximate different real caloric materials. The performance of each material is assessed under conditions that are relevant for near-room-temperature applications, such as air-conditioning or refrigeration. The main goal is to assess the effect of hysteresis on a caloric cooler’s performance and efficiency as a function of the caloric properties, regardless of the type of caloric effect. This has not yet been done in such a comprehensive way and is crucial for further designing of caloric devices and appropriate caloric material selection. The caloric effect is treated in a generic way, where the caloric material experiences an entropy generation associated with a change in the field. Practical details, such as how large a field can be applied (in the form of a magnetic field, mechanical strain, etc.), are not considered in this article. Rather, the goal is to assess the caloric properties regardless of the specific type of field that is applied.

2. METHODOLOGY

Although the refrigerants and driving effects are different for each cooling technology, they all operate on the same thermodynamic principle (Kitanovski et al., 2015a). A cooling cycle can be built by applying a field or combination of fields to the caloric material, causing its temperature to increase, then the heat is rejected while the field is applied, typically using convective heat transfer. The field is then released, causing the material to cool below its
original temperature. Then a cooling load is absorbed by the caloric material, again via convection. The performance of the cooling cycle is commonly represented by the coefficient of performance (COP), which is the ratio of cooling effect to input work. The input work for caloric coolers is typically a motor to apply the field and a pump to provide convection between the fluid and solid caloric material. The COP (or first-law efficiency) is defined as:

\[
COP = \frac{Q_c}{W_{\text{motor}} + W_{\text{pump}}},
\]

where \(Q_c\) is the cooling power, \(W_{\text{motor}}\) is the input motor power and \(W_{\text{pump}}\) is the input pump power. The ideal or reversible Carnot COP for a cooling cycle, which is the maximum performance that can be obtained by the cooling system, can be calculated as:

\[
COP_{\text{ideal}} = \frac{T_c}{T_H - T_c},
\]

where \(T_c\) is the cold reservoir temperature and \(T_H\) is the hot reservoir temperature. The second-law efficiency, \(\eta_H\), is a measure of the actual cooling performance relative to the performance under reversible conditions and is given by:

\[
\eta_H = \frac{COP}{COP_{\text{ideal}}},
\]

A thorough review of caloric material properties is outside the scope of this work, but a representative sample of solid-state refrigerants showing one of the four caloric effects considered for refrigeration (i.e., magnetocaloric, electrocaloric, elastocaloric and barocaloric effect) is given in Table I. Gadolinium (Gd), the benchmark magnetocaloric refrigerant, with a second-order phase transition (SOPT), has essentially no hysteresis (Gutfleisch et al., 2016). The other materials selected are refrigerants with a first-order phase transition that exhibit a caloric effect with the presence of thermal hysteresis and field hysteresis effects. For example, the barocaloric refrigerant neopentyl glycol shows a large pressure-driven thermal change due to reconfiguration of molecules despite hysteresis (Lloveras et al., 2019). It has also been shown that the magnetocaloric Mn-Fe-P-As compound exhibits a magnetic and thermal hysteresis (Engelbrecht et al., 2013). Table I is also the basis for the model materials used in this study that have different sets of constant caloric properties (i.e., specific heat at zero field and maximum isothermal entropy change). The specific heats listed in Table I are average baseline values from previously published studies to give an overall comparison between materials. In operation, specific heats can depend strongly on temperature and applied external field. It should be emphasized that these values are taken from property measurements that are collected in different manners. Engelbrecht et al., (2013) have also shown that the specific heat depends on the thermal history of the caloric material, i.e., there are different distinct cooling and heating curves for specific heat (and magnetization).

It is difficult to give a fair comparison across caloric materials because the method of measuring properties varies with the applied field. Some properties are measured directly,
while many are calculated using Maxwell relations or derived thermodynamically. In some
cases, where $\Delta s_{\text{hys}}$ was not published directly, it has been calculated as a difference between
the positive entropy change (during application of external field) and negative entropy change
(during removal of external field) or from the (isothermal) hysteresis loops using the
following equations:

$$\Delta s_{\text{hys,MC}} = \Delta s_{\text{mag}} - \Delta s_{\text{demag}} = \frac{1}{\rho T} \oint M dB,$$

(4)

where $M$ is the magnetization (A.m$^{-1}$) and $B$ the magnetic flux density (T).

$$\Delta s_{\text{hys,EC}} = \Delta s_{\text{pol}} - \Delta s_{\text{depol}} = \frac{1}{\rho T} \oint P dE,$$

(5)

where $P$ is the polarization density (C.m$^{-2}$) and $E$ the electric field strength (V.m$^{-1}$).

$$\Delta s_{\text{hys,EC}} = \Delta s_{\text{load}} - \Delta s_{\text{unload}} = \frac{1}{\rho T} \oint \varepsilon d\sigma,$$

(6)

where $\varepsilon$ is the strain (%) and $\sigma$ is the stress (MPa).

$$\Delta s_{\text{hys,BC}} = \Delta s_{\text{press}} - \Delta s_{\text{depress}} = \frac{1}{\rho T} \oint V dp,$$

(7)

where $V$ is the volume (m$^3$) and $p$ is the pressure (Pa).
Table I: Summary of caloric properties for magnetocaloric (MC), electrocaloric (EC), elastocaloric (eC), and barocaloric (BC) materials. Values are measured using different techniques depending on the applied field, which can cause variation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phase transition</th>
<th>( \Delta T_{\text{max}} ) (K)</th>
<th>( C_v ) (J kg(^{-1}) K(^{-1}))</th>
<th>( T_{\text{Curie}} ) (K)</th>
<th>( \Delta T_{\text{hys}} ) (K)</th>
<th>( \Delta T_{\text{hys}}/\Delta T_{\text{max}} ) (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MCM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>SOPT</td>
<td>3.1 270</td>
<td>293</td>
<td>1 T</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GdSiGe</td>
<td>FOPT</td>
<td>3.5 270</td>
<td>268</td>
<td>1.5 T</td>
<td>55 Am(^{-1}) kg(^{-1})</td>
<td>4</td>
<td>0.11 0.64</td>
</tr>
<tr>
<td>MNFe(P,As)</td>
<td>FOPT</td>
<td>3.1 550</td>
<td>298</td>
<td>1.5 T</td>
<td>6.5 Am(^{-1}) kg(^{-1})</td>
<td>1.6</td>
<td>0.01 0.08</td>
</tr>
<tr>
<td><strong>ECM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(Mg(<em>{1/3}) Nb(</em>{2/3}))O(_{3})</td>
<td>FOPT</td>
<td>2.5 320</td>
<td>300</td>
<td>90 kV cm(^{-1})</td>
<td>1x10(^{-3}) C m(^{-2})</td>
<td>n/a</td>
<td>1.5x10(^{-3}) 0.06</td>
</tr>
<tr>
<td>P(VDF-TrFE-CFE)/PMN-PT nanocomposites</td>
<td>FOPT</td>
<td>25 1060</td>
<td>300</td>
<td>150 kV cm(^{-1})</td>
<td>n/a</td>
<td>n/a</td>
<td>0.9 1</td>
</tr>
<tr>
<td><strong>eCM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiTi (stabilized at 70°C)</td>
<td>FOPT</td>
<td>28.6 430</td>
<td>340</td>
<td>800 MPa 5.7%</td>
<td>77 MPa</td>
<td>12</td>
<td>1.25 3.6</td>
</tr>
<tr>
<td>NiTi (stabilized at 40°C)</td>
<td>FOPT</td>
<td>24.5 430</td>
<td>310</td>
<td>600 MPa 6%</td>
<td>160 MPa</td>
<td>n/a</td>
<td>3.9 n/a</td>
</tr>
<tr>
<td>CuZnAl</td>
<td>FOPT</td>
<td>16.9 430</td>
<td>310</td>
<td>80 MPa 5.7%</td>
<td>13 MPa</td>
<td>5</td>
<td>0.3 1.3</td>
</tr>
<tr>
<td>Ni(<em>{50})Mn(</em>{31.5})Ti(<em>{18.5})B(</em>{23})</td>
<td>FOPT</td>
<td>31.5 470</td>
<td>300</td>
<td>400 MPa 7%</td>
<td>80 MPa</td>
<td>n/a</td>
<td>2.4 5.3</td>
</tr>
<tr>
<td><strong>BCM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neopentyl glycol</td>
<td>FOPT</td>
<td>42.5 2000</td>
<td>340</td>
<td>0.57 GPa</td>
<td>n/a</td>
<td>20</td>
<td>8.5 1.5</td>
</tr>
</tbody>
</table>

d - directly measured; i – indirectly measured.
2.1 HYSTERESIS IN CALORIC MATERIALS

First-order phase transition materials are generally considered as the most attractive caloric refrigerants due to their high entropy changes, but they also typically have some hysteresis associated with their caloric effect (Mañosoa et al., 2008; Pecharsky and Gschneidner, 1997). Perhaps the easiest form of hysteresis to visualize is that associated with elastocaloric materials. The stress in the wire is lower for a given strain when the NiTi sample is released compared to when it is strained. This means that the work recovered upon release of the sample is lower than that done on the sample to strain it. Part of the input work is dissipated in the sample, which will act to heat the sample. It was shown experimentally that the adiabatic temperature change ($\Delta T_{ad}$) is higher when the sample is strained (J. Tušek et al., 2015a). Similar hysteresis loops occur in other applied fields. Hysteresis in caloric materials harms system performance in two ways: the work associated with the hysteresis reduces efficiency, and the internal heating reduces the cooling potential.

Although hysteresis effects have the potential to greatly decrease caloric cooling performance, there is relatively little reporting of hysteresis properties of caloric materials, and hysteresis values have large variations. Researchers tend to focus on desirable properties such as maximum isothermal entropy change ($\Delta s_{iso,max}$) while ignoring properties whose impact is not as direct. Since the effect of hysteresis on caloric cooling performance is not well understood and because a wide range of reliable data is not available for detailed modeling, model materials with different sets of caloric properties are used in this study. These properties allow the effect of hysteresis to be isolated and modeled for a range of base materials.

Model materials have previously been used to study the effects of magnetocaloric materials on magnetic coolers (Engelbrecht and Bahl, 2010), and a technique for including hysteresis heating in a magnetocaloric regenerator model has been previously reported (Brey et al., 2014). As suggested by Brey et al., (2014), the hysteresis term is treated as an entropy generation term according to Eq. (8).

$$dq_{hys} = T_s \Delta s_{hys} dF,$$

where $q_{hys}$ is the specific heat generation associated with hysteresis, $T_s$ is the temperature of the solid refrigerant, $\Delta s_{hys}$ is the field-dependent entropy generation related to the hysteresis of the material (calculated with Eq. (4)-(7)), and $F$ is the applied field to generate the caloric effect. The treatment of the hysteresis in this article can be considered a worst-case scenario from an efficiency standpoint for hysteresis effects in caloric materials because the reported hysteresis does not necessarily manifest itself as dissipated work for some materials but
rather a reduction in practical caloric properties. Some materials may exhibit higher efficiency in practical operation than predicted here.

The system performance is evaluated for a caloric cooler using six base materials that are summarized in Table II. All materials are designed for a generic applied field, and the $\Delta s_{iso}$ value is the isothermal entropy change from zero field to a given applied field. The materials are considered to have a constant specific heat at zero field and constant $\Delta s_{iso,max}$. Constant specific heat at zero field (presented in Table II) is taken as a baseline value, the specific heat in field is calculated from the material’s entropy properties as a function of temperature and applied field (Eq. 9).

$$c_F = T \left( \frac{\partial s}{\partial T} \right)_F.$$  

Furthermore, an assumption of constant entropy change over a wide temperature range is used in the model. This is reasonable for most first-order caloric materials, except for magnetocalorics, where applying layered regenerators using magnetocaloric materials with slightly different Curie temperatures can increase temperature range of magnetocaloric materials (Bahl et al., 2017; Jacobs et al., 2014).

Each material is modeled with hysteresis entropy generation values ($q_{hys}$) of 0%, 0.04%, 0.5%, 1%, 2%, 6%, and 12% of the total isothermal entropy change. The result of the hysteresis will be an increase in the adiabatic temperature change when the field is applied and a reduced adiabatic temperature change when the field is removed. The materials are not meant to represent specific materials from the literature, but comparing values in Table I and Table II shows that the chosen properties are generally in line with reported material properties.

Table II: Base mode material properties. All materials have a constant specific heat at zero field and constant $\Delta s_{iso,max}$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$c_{av,0field}$</th>
<th>$\Delta s_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low specific heat, low $\Delta s_{iso}$ (LoCLoS)</td>
<td>300 J·kg$^{-1}$·K$^{-1}$</td>
<td>5 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>Low specific heat, medium $\Delta s_{iso}$ (LoCMeS)</td>
<td>300 J·kg$^{-1}$·K$^{-1}$</td>
<td>30 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>Low specific heat, high $\Delta s_{iso}$ (LoCHiS)</td>
<td>300 J·kg$^{-1}$·K$^{-1}$</td>
<td>50 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>High specific heat, low $\Delta s_{iso}$ (HiCLoS)</td>
<td>1000 J·kg$^{-1}$·K$^{-1}$</td>
<td>5 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>High specific heat, medium $\Delta s_{iso}$ (HiCMeS)</td>
<td>1000 J·kg$^{-1}$·K$^{-1}$</td>
<td>30 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
<tr>
<td>High specific heat, high $\Delta s_{iso}$ (HiCHiS)</td>
<td>1000 J·kg$^{-1}$·K$^{-1}$</td>
<td>50 J·kg$^{-1}$·K$^{-1}$</td>
</tr>
</tbody>
</table>
### 2.2 NUMERICAL MODELING

A 1D active regenerator model has been implemented in this study, where the regenerator is treated as a porous medium and correlations are used to determine parameters such as heat transfer between the caloric material and heat transfer fluid and pressure drop through the regenerator bed. The model was originally developed for magnetic refrigeration (Engelbrecht and Bahl, 2010), but here it is generalized for caloric effects using the approach suggested by Planes et al., (2014) and by adding the hysteresis term from Eq. (8) to the solid phase governing equation. The pressure drop term in the fluid governing equation has been ignored in this article to eliminate pressure drop effects from specific regenerator geometries. The governing equations for the solid caloric material and the fluid are given in Eq. (10) and (11), respectively. The 1D numerical model was implemented in MATLAB R2019a. The tolerance value, the number of time and spatial steps were chosen to be high enough that it did not show significant differences in the results. The equations are considered only in the fluid flow direction.

\[
\frac{\partial}{\partial x} \left( k_{\text{stat}} A_c \frac{\partial T_s}{\partial x} \right) + \frac{Nu}{D_h} a_s A_c \left( T_f - T_s \right) = A_c (1 - \varepsilon) \rho_s \left[ c_f \frac{\partial T_f}{\partial t} + T_s \left( \frac{\partial s}{\partial F} \right)_{T_s} \frac{\partial F}{\partial t} + T_s \Delta s_{hys} \frac{\partial s}{\partial t} \right]
\]

\[
\frac{\partial}{\partial x} \left( k_{\text{disp}} A_c \frac{\partial T_f}{\partial x} \right) = \dot{m}_f c_f \frac{\partial T_f}{\partial t} - \frac{Nu}{D_h} a_s A_c \left( T_f - T_s \right) = A_c \phi \rho_f c_f \frac{\partial T_f}{\partial t},
\]

where \( k \) is thermal conductivity, \( T \) is temperature, \( \rho \) is density, \( c_f \) is specific heat of the heat transfer fluid, \( c_F \) is the specific heat of the caloric material at constant field, \( s \) is specific entropy, \( A_c \) is cross-sectional area, \( a_s \) is specific area, \( \phi \) is porosity, \( x \) is axial positon, \( t \) is time, \( \dot{m} \) is mass flow rate, \( F \) is the internal field, and \( Nu \) is the Nusselt number. The Nusselt number is calculated by the correlation given by Kaviany, (1995) (Eq. (12)) determining the heat transfer between a packed sphere bed regenerator and the fluid. The subscripts \( f \) and \( s \) represent fluid and solid refrigerant, respectively. The static conductivity denoted as \( k_{\text{stat}} \) is the effective thermal conductivity of the whole regenerator bed, when there is no fluid motion. It is included in the energy balance of the solid caloric material (Eq. (10)). The dispersion-related conductivity, \( k_{\text{disp}} \), is used to compute conduction in the fluid energy balance (Eq. (11)), as dispersion causes the mixing of fluid along the regenerator bed in the flow direction. The Nusselt number is a function of Reynolds number (\( Re \)) and Prandtl number (\( Pr \)). They are given in Eq.(13) and Eq.(14), where \( \eta_f \) is the fluid dynamic viscosity.

\[
Nu = 2 + 1.1 Re^{0.6} Pr^{1/3}
\]
As described in (Engelbrecht and Bahl, 2010), the governing equations are discretized over a numerical grid of uniform times steps over one full cycle and spatial steps across the regenerator bed. The model takes fully implicit time steps to evaluate the temperature at each spatial node in the regenerator throughout a full cycle, and material properties and heat transfer characteristics are recalculated for each time step. The model runs until cyclical steady state is achieved, meaning the temperature through the regenerator at the beginning of the cycle is the same as at the end of the cycle within a numerical tolerance. It should be noted that half of the hysteresis heating in the solid material occurs on application and other half on the removal of the applied field.

Several important assumptions were made in the development of the model. First, the heat transfer fluid and caloric material are incompressible and the mass flow rate is assumed to be perfectly distributed over the cross-section of the regenerator, meaning there is no spatial variation in the flow within the regenerator bed. The caloric material and porosity in the regenerator are assumed evenly distributed. The model used in this study assumed that all dissipative energy due to hysteresis goes into heat (and not sound or other vibrations). Pressure drop was not considered in this study, as the estimation of the pressure drop is more relevant to a regenerator geometry study. Ignoring the pressure drop across the regenerator bed simplifies the equation for the COP (Eq. (1)), as the pump work will be zero. The efficiency of the electrical motor (or any other device) that applies the external field is assumed to be 1. Thus, the modeled COPs are for the shaft power applied to the system. Valves, controlling the fluid flow during the cold and hot blow are not considered in the model.

The regenerator bed has a uniform geometry (i.e., the bed porosity does not vary spatially). As the study focuses on the effect of the hysteresis, the same geometry is considered for all caloric effects in order to eliminate the effect of geometry. Regenerator housing effects on the cooling performance were not modeled (i.e., the model assumes adiabatic boundary conditions). The field is applied and removed with a linear ramp (see Fig. 1).
Fig. 1: Applied external field and applied volumetric fluid flow rate profiles as a function of time for a 2 Hz cycle.

System performance will depend on the amount of caloric material, the regenerator geometry, fluid flow rate, cycle frequency, temperature span, Nusselt number and other parameters. To keep the modeling parameter space at a practical level while still exploring the effects of material properties, the regenerator geometry is fixed in this article (fixing the volume of caloric material), as mentioned earlier. The fluid flow rates and cycle frequency are allowed to vary. The characteristics of the regenerator and operating conditions are listed in Table III. A similar regenerator geometry was modeled by Engelbrecht and Bahl, (2010). The dwell ratio is the fraction of the cycle when there is no fluid flow for a given regenerator bed. The delay time is the time from the beginning of the field application process before the blow period begins. The material properties (except the specific heat) are temperature-independent, so the absolute temperature does not affect performance. The Carnot COP is 9.1 for the operating conditions listed in Table III. The applied external field and volumetric fluid flow profiles are shown in Fig. 1. Both profiles are aligned such that the entire hot-to-cold blow occurs while the entire regenerator experiences the maximum applied field. Improved performance could be achieved by optimizing the field and flow profiles (Kitanovski et al., 2014), but the overall comparison of material properties is expected to remain the same.
Table III: Input parameters for the numerical model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat transfer medium</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>Temperature span</td>
<td>30</td>
<td>K</td>
</tr>
<tr>
<td>Hot end temperature</td>
<td>303</td>
<td>K</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>295</td>
<td>K</td>
</tr>
<tr>
<td>Motor efficiency</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Pressure drop</td>
<td>0</td>
<td>Pa</td>
</tr>
<tr>
<td>Pump work</td>
<td>0</td>
<td>W</td>
</tr>
<tr>
<td>Cycle frequency</td>
<td>varied</td>
<td>Hz</td>
</tr>
<tr>
<td>Cycle time, $\tau_{cycle}$</td>
<td>varied</td>
<td>s</td>
</tr>
<tr>
<td>Fluid flow rate</td>
<td>varied</td>
<td>m$^3$.s$^{-1}$</td>
</tr>
<tr>
<td>Delay time</td>
<td>$15/360*\tau_{cycle}$</td>
<td>s</td>
</tr>
<tr>
<td>Flow ramp period for fluid flow</td>
<td>0.1</td>
<td>s</td>
</tr>
<tr>
<td><strong>Regenerator characteristics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length of regenerator</td>
<td>60</td>
<td>mm</td>
</tr>
<tr>
<td>Cross-section of regenerator, $A_c$</td>
<td>400</td>
<td>mm$^2$</td>
</tr>
<tr>
<td>Volume of regenerator, $V$</td>
<td>24</td>
<td>cm$^3$</td>
</tr>
<tr>
<td>Regenerator type</td>
<td>packed sphere</td>
<td></td>
</tr>
<tr>
<td>Particle diameter</td>
<td>0.4</td>
<td>mm</td>
</tr>
<tr>
<td>Number of beds</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Bed porosity, $\phi$</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Refrigerant density, $\rho_s$</td>
<td>8000</td>
<td>kg.m$^{-3}$</td>
</tr>
<tr>
<td>Refrigerant mass, $m$</td>
<td>123</td>
<td>g</td>
</tr>
<tr>
<td>Refrigerant thermal conductivity, $k_s$</td>
<td>10</td>
<td>W.m$^{-1}$.K$^{-1}$</td>
</tr>
</tbody>
</table>

3. RESULTS AND DISCUSSION

A set of typical performance curves for one representative model material operating at a single frequency of 1 Hz and a fixed temperature span of 30 K is shown as a function of utilization factor in Fig. 1. The utilization is the ratio between the thermal capacity of the fluid that moves into the regenerator and the thermal capacity of the solid refrigerant. The plot presents the regenerator cooling characteristics, i.e., the COP and the specific cooling power, which is the cooling power generated per mass of solid refrigerant, for different values of $q_{hys}$. It is evident from Fig. 2 that the regenerator cooling characteristics for LoCLoS are highly dependent on the utilization factor and hysteresis value. For each hysteresis value, an optimum specific cooling power, which is the peak of the curve, can be determined along with a corresponding COP (see also Fig. 5 and Fig. 6). All modeling raw data for each model material can be accessed at Masche et al., (2020).
Fig. 2: Specific cooling power (left axis) and corresponding COP (right axis) as a function of utilization of different hysteresis entropy generation values \( (q_{hys}) \) for LoCLoS operating at 1 Hz. Plots only show positive specific cooling loads and COPs. Cooling power is plotted with solid lines, while COP is plotted with dashed lines.

The specific cooling power and the COP increase with increasing utilization factor until they reach a maximum, as seen in Fig. 2, and the maximum COP occurs at a lower utilization factor than the maximum cooling power. As the utilization increases above the maximum COP and the maximum \( q_{hys} \), the system cooling performance decreases. Fig. 2 only presents positive specific cooling powers and COPs. For example, the specific cooling power for LoCLoS with a \( q_{hys} \) of 2% reaches negative values (meaning that the regenerator cannot sustain the specified temperature span) at utilization factors above 1.9. Similarly, plots for \( q_{hys} \) of 6% and 12% are not shown, as the modeled cooling powers and COPs are negative, indicating that the required temperature span of 30 K cannot be established. The influence of the utilization factors on the regenerator cooling performance has been also discussed in detail in Kitanovski et al., (2015c).

The trends shown in Fig. 2 are similar to those for all model cases in this work, although the sensitivity of each model material to the hysteresis entropy generation value varies. Fig. 3 and Fig. 4 show that the cooling performance of all model materials is greatly affected by hysteresis. As hysteresis increases, the specific cooling power and cooling COP decreases in each material. The influence of hysteresis on the COP is more dramatic than on cooling power. Because the work input for efficient caloric coolers is quite low, the COP values fall...
quickly as hysteresis increases due to the reduced cooling power and the increased work input.

The cooling performance maps in Fig. 3 and Fig. 4 also show that materials with lower specific heat ($c_{av,0\text{field}} = 300 \, \text{J.kg}^{-1}.\text{K}^{-1}$) are less sensitive to hysteresis than materials with higher specific heat ($c_{av,0\text{field}} = 1000 \, \text{J.kg}^{-1}.\text{K}^{-1}$). The larger $\Delta T_{ad}$ associated with a lower specific heat increases the heat transfer in the regenerator, which improves regenerator performance and overall system performance, even when hysteresis is present. This is positive from a cooling device-performance point of view, as materials with lower specific heat will introduce fewer losses in each cooling cycle. Furthermore, it can be seen that the COP decreases with increasing $\Delta s_{iso}$ for materials with no or minor hysteresis. On the other hand, for materials with higher hysteresis, the COP is better at larger $\Delta s_{iso}$, indicating that materials with higher $\Delta s_{iso}$ are less sensitive to hysteresis. The cooling performance maps in Fig. 3 and Fig. 4 also show that materials with higher caloric effect would perform much more efficiently at higher specific cooling powers.
Fig. 3: Cooling performance maps (cooling COP vs. specific cooling power) for the model materials LoCLoS (a), LoCMcS (b), and LoCHiS (c) with low specific heat ($c_{av,\text{field}} = 300 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) at a cycle frequency of 1 Hz. Plots show only positive specific cooling loads and COPs, and thus negative values are not presented. The COP is plotted with solid lines, while the second-law efficiency is plotted with dashed lines.
Fig. 4: Cooling performance maps (cooling COP vs. specific cooling power) for the model materials HiCLoS (a), HiCMeS (b), and HiCHiS (c) with high specific heat \( c_{av,\text{field}} = 1000 \text{ J kg}^{-1} \text{K}^{-1} \) at a cycle frequency of 1 Hz. Plots show only positive specific cooling loads and COPs, and thus negative values are not presented. The COP is plotted with solid lines, while the second-law efficiency is plotted with dashed lines.

Fig. 5a and b show the modeled maximum (optimum) specific cooling power for two representative materials (i.e., LoCMeS and HiCMeS) as a function of cycle frequency and hysteresis value. The cooling performance was modeled for operating frequencies of up to 4 Hz. The limit of 4 Hz was selected because many cooling prototypes operate with frequencies at or below 4 Hz (Kitanovski et al., 2014). For each frequency and hysteresis value, there is a maximum cooling power. The figures also show that the hysteresis value and frequency affect both materials differently. The general trend is that the maximum cooling power increases with increasing cycle frequency. As hysteresis increases, both materials
show a reduction in the maximum cooling power. The material with higher specific heat (i.e., HiCMeS) is more sensitive to hysteresis, as higher hysteresis values lead to a greater reduction of the cooling performance. This reduction is even more pronounced as the cycle frequency increases, as the increased frequency is accompanied by increased internal heating of the material due to hysteresis. For example, for HiCMeS, a frequency of 3.5 Hz and the presence of a very high hysteresis value of 12% can even nullify the caloric effect entirely, as the material is not able to reach a positive cooling power and/or COP. Thus, materials with lower specific heat exhibit improved cooling performance, even including hysteresis. It should be mentioned that the corresponding COPs at the maximum cooling power (Fig. 5) are relatively low compared to the maximum COPs for these two materials, as shown in Fig. 6a and b.

When no hysteresis is present, the maximum COP decreases with increasing cycle frequency. At low cycle frequencies, the heat transfer medium has ample time to exchange heat with the caloric material, leading to high COPs. However, as the cycle frequency increases, the time for heat transfer decreases, reducing the efficiency. The material with a higher specific heat (i.e., HiCMeS) has higher modeled maximum COPs for each frequency. However, with the presence of hysteresis, the maximum COPs for LoCMeS and HiCMeS greatly decrease. HiCMeS ($c_{av,0field} = 1000 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, $\Delta s_{iso} = 30 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) shows a larger percentage reduction of the modeled COPs (and thus efficiency) than LoCMeS ($c_{av,0field} = 300 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, $\Delta s_{iso} = 30 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$), even when a small hysteresis value (i.e., 0.5% of $q_{hys}$) is present. Thus, HiCMeS is more sensitive to hysteresis. On the other hand, LoCMeS can tolerate some level of hysteresis without compromising the regenerator efficiency drastically.

![Fig. 5: Modeled maximum cooling power (solid lines) and corresponding COP (dashed lines) for LoCMeS (a) and HiCMeS (b) as a function of cycle frequency for different hysteresis values. Plots only show data, where the material reaches positive cooling power.](image-url)
Fig. 6: Modeled maximum COP (solid lines) and corresponding cooling power (dashed lines) for LoCMeS (a) and HiCMeS (b) as a function of cycle frequency for different hysteresis values. Plots only show data, where the material reaches positive cooling powers and/or COPs.

In the Supplementary Material, Fig. S1 and S2, and Table S1 summarize the modeled COPs for all materials with and without the presence of hysteresis for two design cooling powers. Two design cooling powers were chosen; 50 W, which can be reached by most model materials, and 300 W, which can be reached only by the best-performing materials. The regenerator materials with the highest COPs for these two design points can then be determined. Cooling devices often have a specific design cooling power where they generally operate. Thus, the best regenerator material has the highest COP at the design cooling power. The general trend is that all materials show the highest COPs when no hysteresis is present and at the lowest working frequency due to the long duration of the fluid flow period, which results in improved heat transfer. The modeled COPs also decrease with increasing operating frequencies, as shown also in Fig. 6.

The value of the material’s isothermal entropy change also affects its sensitivity to hysteresis. Materials with a relatively low entropy change ($\Delta s_{iso} = 5 \text{ J\cdot kg}^{-1}\cdot\text{K}^{-1}$) are very sensitive to the hysteresis entropy generation. Even small hysteresis ($q_{hys} = 0.04\%$) can significantly reduce the system efficiency, to the extent that the cooling device cannot compete with current technologies. Materials with higher $\Delta s_{iso}$ ($\Delta s_{iso} = 50 \text{ J\cdot kg}^{-1}\cdot\text{K}^{-1}$) are capable of tolerating some level of hysteresis in the caloric material, and they can achieve the design cooling power at high working frequencies despite large hysteresis values of 12%. The HiCLoS represents the model material with the lowest regenerator performance, as it is not able to reach the design cooling powers of 50 and 300 W regardless of operating frequency.
and hysteresis entropy generation value. The undesired hysteretic behavior of FOPT materials may be tuned by changing their compound concentration (Kitanovski et al., 2015b). However, the tuning can both change the character of the phase transition, which is usually accompanied by a reduction of the caloric effect, and it can make the material brittle (Gutfleisch et al., 2016).

4. CONCLUSIONS

Intrinsic hysteresis in materials with a first-order phase transition is a large issue that limits their application in solid-state cooling devices. This paper shows that hysteresis can have a large impact on the system performances depending on the caloric properties of the material. For materials with moderate or low isothermal entropy change, even a small amount of hysteresis can limit the adiabatic temperature change under operation and thus considerably reduce the cooling performance, especially the COP, of the device. It has been shown that, for example, for a caloric material with low specific heat and low $\Delta s_{\text{iso}}$ (LoCLoS), increasing the hysteresis entropy generation ($q_{\text{hys}}$) from 0.5 to 1% could decrease the COP by 50% and the cooling power by 20%. Modeling results show that the energy loss in an active caloric regenerator due to hysteresis entropy generation is significantly affected by the materials’ physical (and thermodynamic) properties and working frequency. Materials with high isothermal entropy change and low specific heat (LoCHiS) show less sensitive hysteretic behavior, as they can tolerate high hysteresis entropy generation rates, even at higher working frequencies. Materials with low isothermal entropy change are very sensitive to hysteresis. LoCLoS materials show better performances than LoCMeS (i.e., low specific heat and medium $\Delta s_{\text{iso}}$) and LoCHiS with no hysteresis. When adding just 2% $q_{\text{hys}}$, the COP of LoCLoS decreases by 60%, whereas the decrease of LoCHiS and LoCMeS is only 10% and 20%, respectively. On the contrary, the caloric materials with high specific heat do not tolerate the increase in hysteresis. For example, LoCLoS can tolerate up to 2% $q_{\text{hys}}$ without affecting the regenerator efficiency remarkably, whereas caloric materials with high specific heat and low $\Delta s_{\text{iso}}$ cannot tolerate more than 0.04% $q_{\text{hys}}$. This is of great importance when designing a cooling device optimized for a specific cooling power and working frequency and selecting the most suitable caloric material. The overall conclusions of this study can be applied to any type of active regenerator and caloric material, and the model described in this paper could be used for a more specific materials and design conditions. Future studies could focus on validating the modeling results with experiments on caloric devices using different caloric effects. The most limiting aspect for the model is having detailed material properties.
that correctly account for hysteresis effects with an adequate accuracy and represent the actual properties experienced in a device.

ACKNOWLEDGEMENTS

This work was in part financed by the RES4Build project, which received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No. 814865. L. Ianniciello and K. Engelbrecht would like to acknowledge the financial support from the Independent Research Fund Denmark (contract 8022-00277B). Dr. J. Tušek would like to acknowledge the Slovenian Research Agency (project Multicaloric cooling: J2- 9253) for supporting this work.

Supplementary material

The supplementary material for this paper can be found online at 10.11583/DTU.11611689.v1.

REFERENCES


Hess, T., Maier, L.M., Bachmann, N., Corhan, P., Schäfer-Welsen, O., Wöllenstein, J.,


active magnetic regenerator for cooling applications – part II: Mathematical modeling and thermal losses. Int. J. Refrig. 72, 206–217.


