Electrocaloric refrigeration: an innovative, emerging, eco-friendly refrigeration technique

C Aprea\textsuperscript{1}, A Greco\textsuperscript{2}, A Maiorino\textsuperscript{1}, C Masselli\textsuperscript{1}

\textsuperscript{1}DIIN, Università di Salerno, via Giovanni Paolo II 132, 84084 Fisciano, Salerno, Italia
\textsuperscript{2}DII, Università degli Studi di Napoli Federico II, P.le Tecchio 80, 80125 Napoli, Italia

Email: cmasselli@unisa.it

Abstract. Nowadays, the refrigeration is responsible of about 15\% of the overall energy consumption all over the world. Actually most of the refrigerant fluids working in vapor compression plants (VCPs) are environmentally harmful, since they presents high GWP (Global Warming Potential), which leads to a substantial warming of both earth surface and atmosphere. Electrocaloric refrigeration (ER) is an innovative, emerging refrigeration technique based on solid state refrigerant that shows a great potential. It fits in the context of environment-friendly refrigeration systems, whom are spreading increasingly to replace VCPs. ER is founded on electrocaloric effect that is a physical phenomenon found in materials with dielectric properties, electrocaloric materials. The thermodynamical cycle that best is addressed to the electrocaloric refrigeration is Active Electrocaloric Regeneration cycle (AER) that consists of two adiabatic and two isofield stages. The core of an electrocaloric refrigerator is the regenerator whom operates both as refrigerant and regenerator in an AER cycle. In this paper, we compare the energetic performance of a commercial R134a refrigeration plant to that of an electrocaloric refrigerator working with an AER cycle. The comparison is performed in term of TEWI index (Total Equivalent Warming Impact) that includes both direct and indirect contributions to global warming.

1. Introduction

Nowadays, the refrigeration is responsible of about 15\% of the overall energy consumption all over the world and most modern refrigeration units are based on Vapor Compression Plants (VCP). The traditional refrigerant fluids, i.e. CFCs and HCFCs, have been banned (Montreal 1987) because of their contribution to the disruption of the stratospheric ozone layer (Ozone-Depleting Potential substances ODPs). Human activities have increased the concentration of greenhouse gases in the atmosphere, thus resulting in a substantial warming of both earth surface and atmosphere. The impact of greenhouse gases on global warming is quantified by their GWP (Global Warming Potential). The Kyoto Protocol (1987) sets binding targets for greenhouse gas emissions. National laws and regulations implementing the Kyoto Protocol differ from one another, but they typically call for a phase down of HFC consumption. Therefore actually most of the refrigerant fluids working in vapour compression plants are environmentally harmful. Near all the efforts done [1] in the identification of new refrigerant fluids, environmental friendly, to be employed in VCP, in the last decades the interest of scientific community has oriented itself in studying and developing new refrigeration technologies.
of low impact in our ecosystem. In a recent past the most promising, eco-friendly, emerging technique seemed to be magnetic refrigeration (MR) [2], whose main innovation consists in employing solid materials as refrigerant, instead of the fluid ones proper of vapour compression. The magnetic refrigerant is a solid, has essentially zero vapour pressure, and therefore it is ecological with no direct ODP and zero GWP [3]. Specifically MR founds its operation on magnetocaloric effect (MCE) [4], a physical phenomenon observed in every material with magnetic properties and it consists in an increment of temperature in the MCE material as a consequence of material’s magnetization under adiabatic conditions. Furthermore, magnetic refrigeration exhibits high cooling efficiencies (30-60% of Carnot COP) [5]. On the other side MR presents at least two relevant disadvantages: the high costs associated both with the magnetic field generation [6-8] and magnetic materials [9]. As alternative to MR and therefore to MCE, a similar caloric effect was detected in some materials by the application of an electric field [10-11] and it is called electrocaloric effect (ECE). Electrocaloric refrigeration (ER) is a refrigeration technology based on solid state refrigerants, exhibiting a relevant ECE, that has shown great potential. Even if, as MR, it doesn't presents any ODP or GWP contribution, such technology results more advantageous than MR since it requires high electric fields, easier and cheaper to be generated than magnetic fields proper of the latter. Moreover a 50% of Carnot limit COP could be achieved with electrocaloric refrigeration in small scale applications. The thermodynamical cycle that best is addressed to the electrocaloric refrigeration is Active Electrocaloric Regeneration cycle (AER) that consists of two adiabatic stages (polarization–depolarization) and two isofield stages, corresponding to the heat transfer fluid flows through the regenerator. The Active Electrocaloric Regenerator (AER) is the core of an electrocaloric refrigerator; it is designed as particular thermal regenerator, made of electrocaloric materials and acting both as refrigerant and regenerator in an AER cycle. This paper compares a commercial VCP employing R134a and an electrocaloric refrigerator, under different values of electric field applied, and testing a number of electrocaloric materials as refrigerant, exhibiting several nano-structural differences in order to provide a general framework as detailed as possible, to identify the eco-compatibility of EMs and to evaluate their environmental impact in terms of a greenhouse effect with respect to a vapor compression plant. The comparison is performed in term of TEWI (Total Equivalent Warming Impact) index that takes into account both direct and indirect contributions to global warming.

2. Electrocaloric effect and the AER cycle

The electrocaloric effect is a physical phenomenon detected in material with dielectrical properties, i.e. electrocaloric materials (EM), which consists in variation of the electrical contribution of the material's entropy as a consequence of an electric field application. The total specific entropy of a particular dielectric material, i.e. an electrocaloric material, consists of three contributions:

$$S = S_{el}(T,E) + S_l(T) + S_e(T)$$

(1)

where: $S_{el}$ represents the electric, $S_l$ the lattice and $S_e$ the electron entropy. When the electric field is applied to an electrocaloric material the electric dipoles become oriented according to the direction of the field. If this is done isothermally, it carries to a decrement of the material’s electric entropy by the isothermal entropy decreasing $\Delta S_T$. On the other side, if the polarization is done adiabatically, with no thermal transfer toward the ambient, the total sample entropy remains constant and the decrease in electric entropy is countered by an increase in the lattice and electron entropy. This causes a heating of the material and it takes an increasing of its temperature given by the adiabatic temperature change, $\Delta T_{ad}$. Dually, an adiabatic depolarization involves the increasing of the material's electric entropy, causing a decreasing in lattice vibrations and by that a temperature decrease. The expression for $\Delta T_{ad}$ of an EM can be evaluated as:

$$\left(\Delta T_{ad}\right)_s = -\int_{E_i}^{E_f} \frac{T}{C_E} \left(\frac{\partial P}{\partial T}\right)_E dE$$

(2)
where the specific heat can be defined as:

$$C_E = T \left( \frac{\delta s}{\delta T} \right)_E$$  \hspace{1cm} (3)

In case of isothermal process the entropy change can be evaluated as:

$$(\Delta S_{el})_T = \int_{E_i}^{E_f} \left( \frac{\partial P}{\partial T} \right)_E dE$$  \hspace{1cm} (4)

At the Curie temperature, where is located its own electrocaloric phase transition (from ferroelectric state to paraelectric state), an EM shows the peak of ECE, in terms of $\Delta T_{ad}$ and $\Delta S_T$. The two possible electrocaloric phase changes that one can observe at the Curie point in electrocaloric materials are the first and the second order. In a first order transition phase the electrocaloric material can achieve a larger ECE than in a second order, due to the jump in the entropy of the material close its Curie temperature. The thermodynamical cycle best fitting to electrocaloric refrigeration is the reverse Brayton cycle [12], which consists of four processes as shown in Figure 1:

- A-B: adiabatic polarization, obtained increasing the electric field intensity from the values $E_A$ to $E_B$; as a consequence, because of electrocaloric effect, an increasing of EM’s temperature, amounting to a $\Delta T_{ad,AB}$ quantity, is registered;

- B-C: heat rejection to an heat sink under a constant electric field $E_B$;

- C-D: adiabatic depolarization, obtained reducing the electric field intensity from the value $E_B$ to $E_A$; as a consequence in the electrocaloric material one can observe a decrement of its temperature quantified in $\Delta T_{ad,CD}$;

- D-A: heat absorption from a heat source under constant electric field $E_A$.

The most used way for heat transferring between the heat source and the heat sinks, in electrocaloric refrigerators, is the employment of a secondary fluid with the purpose to transfer heat from the cold heat sink to the hot one as a consequence of Brayton cycle. In 1982 Barclay introduced [13] an innovative way to consider the reverse Brayton cycle for magnetic refrigeration, through the Active Magnetic Regenerative refrigeration cycle (AMR cycle), concept which has also been extended to electrocaloric refrigeration, through the Active Electrocaloric Regenerative refrigeration cycle, well known as AER cycle. The AER cycle is applied to an AER regenerator made of electrocaloric material whom has the peculiarity to be both refrigerant and regenerator at the same time, whereas a secondary fluids has the function to transfer heat from the cold to the hot end of the regenerator. Substantially every section of the regenerator experiments its own AER cycle, according to the proper working temperature.

Through an AER one can appreciate a larger temperature span across the regenerator. During the entire cycle the electric field varies between a minimum value $E_{MIN}$ and a maximum, $E_{MAX}$. The regenerator works between a hot reservoir at $T_h$ and a cold one at $T_c$. The AER cycle consists of four processes. With reference to Figure 2, during polarization (A) the electric field applied to the regenerator increases its intensity, whereas there the fluid is stationary: as a result an increase of the EM temperature, due to the ECE, is registered. In the cold-to-hot fluid flow process (B), the secondary fluid blows from the cold to the hot end of the regenerator, while the field has kept at a $E_{MAX}$: the fluid absorbs heat from the regenerator, reaching a temperature higher than $T_h$ and the heat is rejected through a hot heat exchanger. The next process is depolarization (C) where, with no fluid flow, the electric field decreases its intensity until reaching $E_{MIN}$: as a consequence, the electrocaloric material decreases its temperature accordingly to the ECE. Lastly the fluid flows from the hot heat exchanger to the cold one (D), while the field is at the value $E_{MIN}$: as a result the fluid, hotter, cools itself by crossing the regenerator, reaching a temperature lower than $T_C$. At this stage the secondary fluid absorbs heat from the cold heat exchanger at $T_C$, producing a cooling load.
3. Electrocaloric materials for AER refrigeration

In the scenario of AER refrigeration at room temperature, electrocaloric materials are classified in three macro-categories: bulk, thin and thick film materials [11]. The use of thin films instead of bulk materials allows the possibility of applying high electric fields with relatively small voltages (higher breakdown electric field) and yielding higher adiabatic temperature variation. In addition, the bulk materials are usually not compatible with the semiconductor integrated circuit technology, which also makes them unsuitable in practical applications. A disadvantage of the thin film is that their overall stored energy and heat-sinking capacity are small due to their mass limitations. Another disadvantage
of thin films is the fact that they are thermally anchored by substrates, which can reduce the cooling power. Within these two groups EMs can be:

- single crystals (bulk materials);
- ceramics (bulk samples, with thickness higher than 100 μm; thick film (with a thickness greater than 10 μm but lower than 100 μm);
- polymers (thick and thin film, with thickness between 10 μm and 1 μm);

Considering ferroelectric polymers among the most promising electrocaloric materials for cooling application because of their versatility, scalability, weight and cost advantages, in this paper it have been selected some relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer, 59.2/33.6/7.2 mol [14,15] with a film thickness between 4 to 6 μm, non stretched and stretched. In particular, stretching is a process which improves the breakdown field of the considering film. The temperature dependence of ECE of the terpolymer films depends critically on the film preparation conditions. Whereas the uniaxially stretched terpolymer films show pronounced temperature dependence of ECE, the non-stretched films exhibit nearly temperature independent ECE from 5 to 45 °C. Besides, large ECE (ΔT>15 °C) can be induced in both films at 30°C and 150 MV/m. Moreover, in this paper the relaxor ferroelectric terpolymer P(VDF-TrFE-CFE), with a composition of 62.3/29.9/7.8 mol% and a Curie temperature of 26°C, it has been considered as the matrix in which bulky chlorine atoms act as random defects to reduce the ferroelectric domain size and the energy barrier to phase transition; BST (Ba0.67Sr0.33TiO3) has been selected as the filler. For Ba0.67Sr0.33TiO3 the ferroelectric-paraelectric transition occurs at 27°C. The ECE of the P(VDF-TrFE-CFE)/BST polymer nanocomposites has been significantly enhanced in comparison to those of the polymer matrix and filler, at relatively low electric field [16]. In the group of ceramics it has been considered a thin film of PbSc0.5Ta0.5O3 (PST), a relaxor ceramic which exhibits a second-order-phase transition. Even if PST materials don’t show one of the higher ECE in terms of ΔTad and ΔS, they have many advantages like low electrical hysteresis and negligible thermal hysteresis [17]. Another material tested in this work is 0.93PMN-0.07PT, which is made of 93% of the relaxor ceramic PbMg1/2Nb1/2O3 (PMN) and 7% of the ferroelectric perovskite PbTiO3 (PT). 0.93PMN-0.07PT thin film exhibits a giant ECE at its Curie temperature of 27°C [18] but it shows a moderate thermal hysteresis at 18°C [19]. Furthermore, another family of ceramic materials has been studied: the Pb1.32La0.5Zr0.85Ti0.15O3 (PLZT) antiferroelectric thick films [20]. Such antiferroelectric films have been deposited on a LNO/Si (1 0 0) substrate. A film with a single composition of PLZT 11/85/15 shows a Curie temperature around 111°C. It is possible to use a compositionally graded structure in order to improve many properties of the EM including dielectric properties, saturation polarization and pyroelectric coefficient. Compared to thick films at single composition, the compositionally graded films show higher dielectric constants and larger saturation polarizations. Therefore, also an improved energy storage performance and a giant ECE are observed. It is possible to define an “up-graded” composition thick films by varying the La content from 8 mol % at the substrate interface, to 14 mol% at the top surface; whereas films with the opposite gradient have been called “down-graded” films. The electric cooling efficiency of an electrocaloric material can be evaluated considering the magnitude of (ΔSΔTad), ΔTad and considering two different parameters: RCP(S) and RCP(T). RCP(S) and RCP(T) represent the relative cooling power in isothermal and in adiabatic processes. They are defined by the following equations:

\[ RCP(S) = \Delta S_{el(max)} * \Delta T_{FWHM} \quad (5) \]

\[ RCP(T) = \Delta T_{ad(max)} * \Delta T_{FWHM} \quad (6) \]

where ΔS_{el(max)} and ΔT_{ad(max)} are the maximum ΔS_{el} and ΔT_{ad} values at a fixed variation of the electric field and ΔT_{FWHM} is the full-width of temperature corresponding to the half of the maximum.

Table 1 summarizes the characteristics of the presented electrocaloric materials in the room temperature range and it allows a quick comparison between the different electrocaloric materials.
PLZTs show peak values of $\Delta T_{ad}$ and $\Delta S_{el}$ always higher than that of the other materials: for PLZT single composition, the peak is out of the room temperature range but for the up-graded and down-graded PLZT materials it is within. In the polymer group, P(VDF-TrFE-CFE)/BST67 shows the higher value of ECE. In terms of RCP(T) and RCP(S), P(VDF-TrFE-CFE)/BST67 is the best one but PLZT up-graded also shows acceptable values. P(VDF-TrFE-CFE) has the lower thermal conductivity and therefore the leakage currents under the applied field are negligible (together with the undesired Joule effect).

| Materials | $T_c$ [°C] | $\Delta E$ [MV/m] | $\Delta T_{ad}$ [°C] | $\Delta S_{el}$ [J/kgK] | $\rho$ [kg/m$^3$] | $k$ [W/mK] | $C_E$ [J/kgK] | RCP(T) [K$^2$] | RCP(S) [J/kg] |
|-----------|-----------|------------------|------------------|------------------|---------------|-------------|--------------|--------------|--------------|
| P(VDF-TrFE-CFE) non stretched | 300 | 70 | 3.8 | 25 | 1800 | 0.2 | 1500 | 355 | 3993 |
| P(VDF-TrFE-CFE) non stretched | 300 | 100 | 7 | 30 | 1800 | 0.2 | 1500 | 657 | 5704 |
| P(VDF-TrFE-CFE) stretched | 300 | 100 | 8 | 30 | 1800 | 0.2 | 1500 | 500 | 4345 |
| P(VDF-TrFE-CFE)/BST67 | 311 | 75 | 9.2 | 80 | 2060 | 1 | 1260 | 1087 | 10530 |
| P(VDF-TrFE-CFE)/BST71 | 322 | 75 | 9.4 | 79 | 2060 | 1 | 1260 | 1038 | 10000 |
| P(VDF-TrFE-CFE)/BST74 | 331 | 75 | 9.7 | 78.5 | 2060 | 1 | 1260 | 1019 | 4065 |
| P(VDF-TrFE-CFE)/BST77 | 337 | 75 | 9.9 | 78 | 2060 | 1 | 1260 | 960 | 4180 |
| PST | 341 | 77.4 | 6.2 | 6.3 | 8800 | 1.1 | 320 | 657 | 693 |
| 0.93PMN-0.07PT | 298 | 50.9 | 9 | 10 | 8300 | 1.384 | 320 | 125 | 135 |
| 0.93PMN-0.07PT | 298 | 72.3 | 13 | 14 | 8300 | 1.384 | 320 | 160 | 162 |
| PLZT 11/85/15 | 111 | 90 | 12 | 10 | 7900 | 1.9 | 330 | 1320 | 1200 |
| PLZT upgraded / | 90 | 28 | 33 | 7900 | 1.9 | 330 | 2800 | 3300 |
| PLZT downgraded / | 90 | 20 | 23 | 7900 | 1.9 | 330 | 1200 | 1380 |

4. The TEWI concept
The impact of greenhouse gases on global warming is quantified by their GWP, defined as the mass of CO$_2$ that would result in the same net impact on global warming as the release of a single unit (kg) of the atmospheric component in question [21]. VCPs produce both a direct and an indirect contribution to global warming. The former depends on the GWP of refrigerant fluids and on the fraction of refrigerant charge released in the atmosphere during operation and maintenance, or not recovered when the system is scrapped. The indirect contribution consists in the so-called energy-related contribution. In fact, a VCP requires electrical energy, produced by a power plant that typically burns a fossil fuel releasing CO$_2$ to the atmosphere, which is a strong function of its COP, of the power plant efficiency and of the fuel used in the conversion plant that affect the emissions per unit energy converted. The Total Equivalent Warming Impact (TEWI) index takes into account both contributions to global warming of the system. The concept of TEWI was developed to combine the effect of direct refrigerant emission with those due to energy consumption and the related combustion of fossil fuels for the electric energy production. TEWI is the sum of the direct contribution of the greenhouse gases used to make the systems or to operate and the indirect contribution of carbon dioxide emissions, resulting from the energy required to run the systems over their normal lifetimes. The TEWI is calculated as:

$$TEWI = CO_{2,dir} + CO_{2,indir} \quad [\text{kg CO}_2] \quad (7)$$
The direct global warming effect of refrigerant fluids, stemming from the absorption they produce of long-wave radiations, depends on their GWP and on the fraction of refrigerant charge released in the atmosphere. The last is mainly due to leakage during the operational plant life time (P_L) and to the residual amounts which, according to the current state of technology, are not recyclable and thus are released to the atmosphere when taking the plant out of operation (1-P_R). In the simulation P_L is assumed as 5%, whereas P_R has not been considered. The literature provides some indicative, average levels of CO_2 release per KWh of electrical energy for various countries. For Italy, the value is 0.6 kg CO_2/kWh. The annual power consumption assumed is 290 kWh per year that corresponds to a commercial medium size wine cooler. R134a is an HFC with zero ODP and a GWP of 1430.

5. Model description

The model presented [22] in this paper is a two-dimensional numerical model of a parallel plates AER regenerator operating at room temperature. The regenerator has a rectangular shape (20x45mm). The area is filled with 54 parallel plates of EM; every plate has a thickness of 0.25mm, in order that it is smaller than the thermal penetration depth \( \delta \) of every material, where \( \delta \) is defined as:

\[
\delta = \sqrt{\frac{k}{\pi f \rho C_E}}
\]

where \( f \), \( k \), \( \rho \) and \( C_E \) are the operating frequency and the thermal conductivity, density and specific heat. The amount of the area occupied by all of the plates is 60% of the total rectangular area. A group of channels is formed by stacking plates in the regenerator area, where the secondary fluid flows. The mathematical formulation that describes the AER cycle includes a number of distinct groups of equations according to the different processes of the AER cycle that the regenerator experiences. The equations that rule the regenerative fluid flow processes, in both directions, are: the Navier-Stokes for the fluid flow and the energy equations for both the fluid and the solid particles. With the assumptions that the fluid is incompressible, laminar and the viscous dissipation neglected, the above equations are:

\[
\begin{align*}
\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} &= - \frac{1}{\rho_f} \frac{\partial p}{\partial x} + v \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \\
\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} &= - \frac{1}{\rho_f} \frac{\partial p}{\partial y} + v \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) \\
\frac{\partial T_f}{\partial t} + u \frac{\partial T_f}{\partial x} + v \frac{\partial T_f}{\partial y} &= \frac{k_f}{\rho_f C_{fp}} \left( \frac{\partial^2 T_f}{\partial x^2} + \frac{\partial^2 T_f}{\partial y^2} \right) \\
\frac{\partial T_s}{\partial t} &= \frac{k_s}{\rho_s C_{sp}} \left( \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial^2 T_s}{\partial y^2} \right)
\end{align*}
\]  

The equations that model the polarization and depolarization processes are:

\[
\begin{align*}
\rho_f C_{fp} \frac{\partial T_f}{\partial t} &= k_f \left( \frac{\partial^2 T_f}{\partial x^2} + \frac{\partial^2 T_f}{\partial y^2} \right) \\
\rho_s C_{sp} \frac{\partial T_s}{\partial t} &= k_s \left( \frac{\partial^2 T_s}{\partial x^2} + \frac{\partial^2 T_s}{\partial y^2} \right) + Q
\end{align*}
\]
They must take into account the ECE which elevates or lowers the temperature of the solid by the variation of the external field applied to the regenerator. Hence the ECE temperature variation $\Delta T_{ad}$ is converted [23] into a heat source $Q$:

$$Q = Q(E, T_s) = \rho \varepsilon_{sp}(H,T_s) \Delta T_{ad}(H,T_s) \frac{dt}{dt}$$

(13)

which has the dimensions of a power density and included in the solid energy equation, only for polarization and depolarization phases. The term $Q$ is positive during polarization, negative during depolarization. $\Delta t$ is the period of the polarization/depolarization process. The coupled equations that govern the AER cycle, imposed on this model, are solved using Finite Element Method. The AER cycle is modeled as four sequential steps. The same time step $\Delta t$ has been chosen for the resolution during all the four periods of the cycle. The cycle is repeated several times with constant operating frequency until the regenerator reaches steady state operation. The refrigeration energy and the energy supplied in the environment are calculated according to the following equations:

$$Q_{ref} = \int_{t_p}^{t_p+t_{CF}+t_{DF}+t_{HF}} \dot{m}_f C_f (T_f - T_f(0,y,t)) \, dt$$

(14)

$$Q_H = \int_{t_p}^{t_p+t_{CF}} \dot{m}_f C_f (T_f(L,y,t) - T_H) \, dt$$

(15)

The work of the secondary fluid circulation pump is:

$$W_p = \frac{\dot{m}(\Delta p_{CF} + \Delta p_{HF})}{\eta_p \rho_f} (t_{CF} + t_{HF})$$

(16)

The Coefficient of Performance is:

$$\text{COP} = \frac{Q_{ref}}{Q_{rej} - Q_{ref} + W_p}$$

(17)

The COP of the vapor compression plant working under the same operating conditions of the above mentioned AER cycle was predicted with the DOE/ORNL Heat Pump model. The VCP used in the simulation is a commercial, small size, R134a refrigerator with a semi-hermetic compressor, air cooled condenser, forced air circulating evaporator [24].

6. Results and discussion

Several AER cycles were simulated with EM, reported in Table 1, employed as refrigerant. In all of the cases, the secondary fluid is pure water. The simulations were performed with fixed AER cycle frequency (1.25 Hz), cold and hot heat exchanger temperature ($T_c=292$ K, $T_e=300$ K). Fluid flow rate was varied in the range $0.034-0.057$ kg/s to characterize the performance sensitivity of the regenerator. The results presented were generated for several electric field applied, in order to provide a general framework. The TEWI direct contribution of an AER cycle is zero because of refrigerant solidity, which has essentially zero vapor pressure and GWP. The direct contribution of the vapor compression plant accounts about 10 % of the whole value. The parameter that mostly affects the TEWI indirect contribution is the COP of the plant. Figure 3, which shown the COP of all the materials presented for different fluid flows rates, reveals that upgraded and downgraded thin film of PLZT materials have the highest COPs. Moreover, also the thin film 0.93 PMN-PT, the relaxor ceramic PST and most of P(VDF-TrFE-CFE)/BST polymer nanocomposites exhibit satisfactory performances.
Figure 3. COP of the tested materials vs fluid flow rate.

Figure 4. (A) ΔTEWI for materials with lower greenhouse effect with respect to a VCP. (B) ΔTEWI for materials with higher greenhouse effect with respect to a VCP.
In order to make a comparison ΔTEWI has been defined according to the following equation:

$$\Delta \text{TEWI} = (\text{TEWI}_{\text{AER}} - \text{TEWI}_{\text{VCP}})/\text{TEWI}_{\text{VCP}}$$ (18)

In Figure 4 is reported ΔTEWI related to all the detected materials, for different fluid flow rates. Figure 4(A) clearly shows that the AER cycle working with these materials has a lower greenhouse effect with respect to a VCP. In particular with upgraded thin film of PLZT ΔTEWI varies between a minimum of -62.5% to a maximum of -39.1%. Figure 4(B) reports all the materials for which the AER cycle shows an environmental impact higher than the VCP one; materials not suitable for an eco-friendly refrigeration.

7. Conclusions

In the present paper, a practical model for predicting the performance and efficiency of an AER refrigerator system for different electrocaloric materials has been introduced. In particular, the relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer, P(VDF-TrFE-CFE)/BST polymer nanocomposites, the 0.93PMN-0.07PT thin film, thick films of PLZT in single, upgraded and downgraded compositions and thin film of the relaxor ceramic PST have been considered as solid refrigerants. In order to make a comparison, the energetic performances of a vapor compression plant, working in the same operating conditions, have been evaluated by means of a computer program. Attention has been devoted to the evaluation of the greenhouse effect of both AER and vapor compression cycle. The greenhouse effect has been evaluated by means of TEWI index. The simulations clearly show that most of the tested materials has a TEWI index always lower than a VCP. In particular upgraded and downgraded PLZT thin films are the best electrocaloric materials because an AER cycle working with them, shows a greenhouse effect lower than that of a traditional plant of around 50%. Also 0.93PMN-0.07PT and P(VDF-TrFE-CFE)/BST71 reveal promising performances in terms of environmental impact. On the other side the tested thin film of PLZT in single composition, the relaxor ferroelectric P(VDF-TrFE-CFE) terpolymer and PST cannot be considered for refrigeration because they show a contribution in term of greenhouse effect greater than a VCP one. These results indicate that electrocaloric refrigeration is a promising refrigeration technology that could be used in cooler applications. An AER refrigerator can be an eco-friendly technology if it is used with electrocaloric materials that show a significant ECE. From a global point of view (performances and environmental impact), the most promising materials are the upgraded and downgraded PLZT thin films, really performing, whom give a contribution to global warming satisfactorily lower than a vapor compression plant one.

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