

Thermodynamics of Phase-Change Energy Storage: The Effects of Undercooling on Entropy Generation During Solidification.

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Abstract

Second law analysis has been applied to an industrial refrigeration phase-change energy storage which consists in the use of a cylindrical tank filled with encapsulated phase-change materials. The paper focuses on the charge mode and more precisely on the effect of undercooling on the entropy production during crystallization. This numerical study is conducted to identify and minimise the thermodynamics losses of the storage process. The dependence of the second law efficiency of the system on various parameters is investigated and discussed.

Key words: phase-change energy storage, charge mode, undercooling, entropy generation.

1. Introduction

Cool Thermal Energy Storage refers to the production and storage of cooling during low load or off-peak electrical periods and the subsequent use of this stored cooling during high load conditions or on-peak electrical periods. Interest in cool-thermal storage has grown substantially in recent years, in particular in the domain of air-conditioning (Arnold, 1987). Thermal energy storage reduces (and sometimes can even eliminate) the need to run the air conditioning compressor during the day when electricity costs are higher.

Following the traditional methodology of heat transfer, the analysis and the design of heat energy storage systems are based completely on First Law considerations. From a First Law perspective, the efficiency of a thermal energy storage system can be assessed in terms of how much thermal energy the system can store. Thus one system is considered to be more effective than another if, for the same energy input in the cold fluid entering the system and the same amount of storage material, it is capable of storing more energy. This approach produces workable designs, but not necessarily those with the highest possible thermodynamic efficiencies. The study

must be based on the Second Law of thermodynamics which shows the degradation of energy by irreversibilities. The approach is based on minimizing the destruction of thermodynamic useful work rather than on maximizing the total amount of thermal energy stored.

This study is the continuation of a work initiated in a previous paper (Strub and Bédécarrats, 1999) that dealt with the discharge mode of a latent heat storage system used in refrigeration processes. The same method based on the numerical calculation of entropy generation (Bejan, 1996) is applied to the charge mode. The results of charge mode cannot be deduced from those of discharge mode because of the undercooling phenomenon.

The phase-change storage process will be briefly reminded as well as the principle of the simulation program of the behaviour of the system. This model is the foundation of the numerical calculation of the variation of the storage volume entropy versus time.

The influence of different parameters on the thermodynamics irreversibilities has been analysed. We lay emphasis on the influence of the undercooling phenomenon during solidification.

2. Description of the Studied Phase-Change Storage System

The presented refrigeration storage process, described at length in a previous paper (Bédécarrats et al., 1996), is a system using encapsulated phase-change materials (PCM). It consists in using plastic spherical containers, whose diameter is 77 mm, filled with PCM. These capsules called nodules are immersed in a chilled fluid in a tank. The PCM inside the containers releases its latent heat and freezes. To discharge the cooling from storage, warm fluid carrying energy from the load flows through the tank, melting the encapsulated PCM.

The charge mode and the discharge mode are not symmetrical because of the undercooling phenomenon. It is well stated that any substance does not crystallize, upon cooling at the melting temperature T_M (liquid-solid equilibrium) but at a lower temperature T . The difference $\Delta T = T_M - T$ is called undercooling. The most important parameter influencing undercooling is the sample size. ΔT increases when the sample size decreases. For example, for water, $\Delta T = 14^\circ\text{C}$ with macrosamples a few cm^3 in volume, but $\Delta T = 36^\circ\text{C}$ with microsamples a few μm^3 in volume (cloud, emulsion...). Even for larger volumes, the undercooling phenomenon is observed. The volume of each nodule is about 200 cm^3 and without precaution, ΔT would be about 9°C . It is however possible to reduce ΔT by addition of nucleating agents. ΔT is less than 3°C with the use of an adequate nucleating agent (Bedecarrats and Dumas, 1997).

The main feature of crystallization is its stochastic character : i.e. samples that are apparently identical will not transform at the same time during the cooling process. This fact is easily explained by the conventional theory of nucleation (Turnbull, 1956), which gives $J(T)$, the probability of crystallization of a sample per unit time.

Previous experimental investigation permits us to define the most effective running of the process : the fluid flows in the tank in order to respect a stratification of isotherms perpendicular to drainage way. When the tank is vertical, the fluid flows from the bottom to the top for the charge process and from the top to the bottom for the discharge process. So the heat transfer fluid temperature depends only on the height.

A numerical simulation that considers the aspects of both the surrounding heat transfer fluid and the phase change material packed inside the nodules has been developed in the cases of the charge and the discharge processes.

In this article, only results concerning the charge process, when the tank is vertical, will be presented. The model, presented in several previous papers (Dumas et al., 1994, Bédécarrats et al., 1996), permits to estimate the crystallization of each nodule, the temperatures in the PCM and in the transfer fluid during the charge process. The tank is divided into several meshes containing N nodules. Even if the heat transfer fluid temperature is considered uniform in each layer, all the nodules of each layer do not simultaneously pass through the phase change at the melting temperature T_M because of the undercooling and the erratic character of the crystallization. The nodules can be in different states (non-crystallized, entirely crystallized or partly crystallized according to their own value of the beginning of the crystallization). Applying the laws of conservation of mass and energy to each layer yields :

$$\rho c_p V \frac{dT}{dt} = \dot{m} c_p (T_i - T_e) + \sum_{i=1}^N \phi_i \quad (1)$$

where $T = (T_i + T_e)/2$ is the average temperature of the heat transfer fluid of the layer (T_i and T_e are respectively the inlet and the outlet temperatures of the layer) and ϕ_i is the flux exchanged by the nodule i depending on the state of the nodule.

Applying the nucleation law, one can calculate the number of new crystallizations Δn and the corresponding fluxes. The number of new crystallizations Δn during the time step Δt is proportional to the probability of crystallization of a nodule per unit time $J(\theta)$ and the nodules remaining unfrozen : $\Delta n = J(\theta)[N - n(t)]\Delta t$. Here $n(t)$ is the number of nodules that have begun to crystallize. For the considered nodules, $J(\theta)$, which depends on the PCM temperature θ , has been determined previously.

The quasi-stationary approximation (Alexiades and Solomon, 1993) is applied to the determination of ϕ_i during crystallization.

Consider a nodule of inner radius r_i . Uniform cooling of its surface will result in a spherically symmetric crystallization-front, $r = r_s(t)$ the inner radius of solid PCM, propagating inwards from $r = r_i$ with liquid at T_M in $0 \leq r < r_s(t)$ and solid in $r_s(t) < r \leq r_i$. Assuming constant thermal properties in each phase, the steady-state solution of the heat conduction in the solid has the form:

$$\theta(r,t) = T_M + [T(t) - T_M] \frac{1 - \frac{r_s(t)}{r}}{\left(\frac{k_s}{k_p} - 1\right) \frac{r_s(t)}{r_i} + \left(\frac{k_s}{hr_c} - \frac{k_s}{k_p}\right) \frac{r_s(t)}{r_c} + 1} \quad (2)$$

The interface conditions here have the standard form :

$$\rho_S L_F \frac{dr_S(t)}{dt} = k_S \left[\frac{\partial \theta(r, t)}{\partial r} \right]_{r=r_S(t)} = \frac{-\phi_i}{4\pi r_S^2(t)} \quad (3)$$

The determination of ϕ_i before crystallization starts and after crystallization is finished is done considering the uniform PCM temperature and one can write that the internal energy variation in the PCM is equal to the flux that leaves the nodule.

To model the presence of the removable covers at the top and the bottom of the tank (two diffusers are assigned to support the nodule and to distribute the chilling fluid flow evenly throughout the tank), additional layers have been considered in which there are no nodules.

The simulation results have been compared with experimental observations (Bédécarrats et al., 1996) with good agreement.

3. Second Law Analysis

From the classical First Law point of view, the efficiency of the system should be expressed in terms of the capability of the system to store energy. This results in the well-known expression for the "First law efficiency" of a thermal energy system given by (Krane, 1987) :

$$\eta_I = \left[\frac{\text{energy actually stored in the tank during the storage period}}{\text{maximum possible energy that could have been stored in the tank during the same period}} \right]$$

It is obvious that the First Law point of view is not sufficient enough to account for the actual performance of the storage process. The energy balance shows only the energy transfer in a system or a process.

Bejan (1978), however, has asserted that the commodity of value is not the energy itself, but the thermodynamic availability of this energy. The maximum reversible work that can be extracted from a given amount of energy is called exergy or availability and it can be destroyed (not conserved) by thermodynamic irreversibilities. Following his pioneering study about the optimisation of a sensible heat storage, the second law techniques have been applied to our case with the help of simulation.

3.1 Entropy generation

The tank which has been well insulated, filled with nodules whose diameter is given, can be considered as an open system. During the charge mode, the fluid enters the system, flows through the nodules and exits warmer. The tank

is the thermodynamic system and is called control volume.

The instantaneous rate of entropy generation \dot{S}_{gen} is calculated from the second law of thermodynamics :

$$\dot{S}_{gen} = \frac{\partial S}{\partial t} - \dot{m}(s_{in} - s_{out}) \geq 0 \quad (4)$$

Because of the low speed of the fluid in the tank, only the effects of heat transfer on entropy production are considered in the present analysis.

Thanks to the model which allows to know the temperatures everywhere in the tank at each time and the different states of the nodules (liquid, solid, partly solid), the entropy variation S of the control volume can be calculated as the sum of entropy variation of all parts in each layer j .

$$\frac{\partial S}{\partial t} = \sum_{j=1}^M \left(\frac{\partial S_{fluid j}}{\partial t} + \sum_{i=1}^N \frac{\partial S_{PCM i,j}}{\partial t} \right) \quad (5)$$

with for the heat transfer fluid :

$$\frac{\partial S_{fluid j}}{\partial t} = \rho c_p V_j \frac{\partial}{\partial t} (\ln T_j)$$

It is important to note that the volume of the flowing fluid takes up about 40% of the volume of the tank.

For the PCM (for the nodule i), before and after crystallization :

$$\frac{\partial S_{PCM i,j}}{\partial t} = m_{PCM} c_{PCM} \frac{\partial}{\partial t} (\ln \theta_{i,j})$$

during crystallization process :

$$\frac{\partial S_{PCM i,j}}{\partial t} = \frac{4}{3} \pi \frac{\rho_S L_F}{T_M} \frac{\partial}{\partial t} (r_{Si,j}^3(t))$$

In this model, we neglect the entropy variation of the plastic capsules.

The rate of entropy transfer $\dot{m}(s_{in} - s_{out})$ can be calculated simply from the inlet and the outlet temperatures of the flowing fluid

The importance of the time-step size used in the numerical modelling is recognised. The accuracy of the results depends on the value of Δt . Δt must be chosen rigorously not to calculate mixing entropy of the fluid introduced by the fact that T is considered the average temperature of the layer. Δt is the step of time which permits the fluid to flow through a layer.

3.2 Entropy generation number

In the same way as in the previous study about discharge mode (Strub and Bedecarrats,

1999) irreversibilities are pointed out by the variation of the entropy generation number N_s . The method is the same and the application for the charge mode is briefly reminded. The reader will refer to the first paper for more details. The entropy generation number N_s has been calculated as the ratio of the destroyed exergy during the time interval 0-t to the exergy stored by the system during the same interval. In other words :

$$\eta_I = \left[\frac{\text{total availability destroyed during the storage period}}{\text{total availability of the cooled fluid stored in the storage unit}} \right]$$

$$N_s = \frac{T_0 \int_0^t \dot{S}_{gen} dt}{\int_0^t \dot{E}x_{cv} dt} \quad (6)$$

$\dot{E}x_{cv}$ is the time rate of change of exergy of the control volume calculated from the time rate of exergy transfer : $\dot{E}x_{in} - \dot{E}x_{out}$ and the time rate of exergy destruction due to irreversibilities within the control volume : $T_0 \dot{S}_{gen}$.

When N_s achieves its maximum possible value of unity, all the availability entering the system is destroyed by irreversibilities. As N_s approaches its lower bound of zero, however, the system approaches completely reversible operation and no availability is destroyed.

In order to compare different situations, the dimensionless number N_s is represented versus the percentage of stored exergy X defined like this :

$$X = \frac{\int_0^t \dot{E}x_{cv} dt}{\int_0^{t_s} \dot{E}x_{cv} dt}$$

where t_s is the complete duration of the storage evaluated when the outlet temperature is the same as the inlet temperature.

3.3 Results from the charge mode

The results concern the charge process where T_{in} remains at a constant value during the process.

3.3.1 Normal undercooling

We begin by focusing attention on the results for a charge mode with the minimum possible value of undercooling. It is important to note that the undercooling cannot be cancelled but can only be reduced. This undercooling is defined by an average value of ΔT of about 2.5 °C.

Extending the investigation at any size of the tank, flow rate and inlet temperature, the variation of N_s versus X is represented for different values of τ and ΔT_{in} defined as :

$$\tau = \frac{\rho V_{cv}}{\dot{m}}$$

representing the time required for the fluid to flow through the tank from the inlet to the outlet. It is independent of the shape of the tank. V_{cv} is the volume of fluid in the tank. In practical cases for the test plant it takes about twenty minutes for the fluid to flow across the tank.

$\Delta T_{in} = T_m - T_{in}$ representing the difference between the inlet and the melting temperature. The melting temperature is constant and equal to 0 °C.

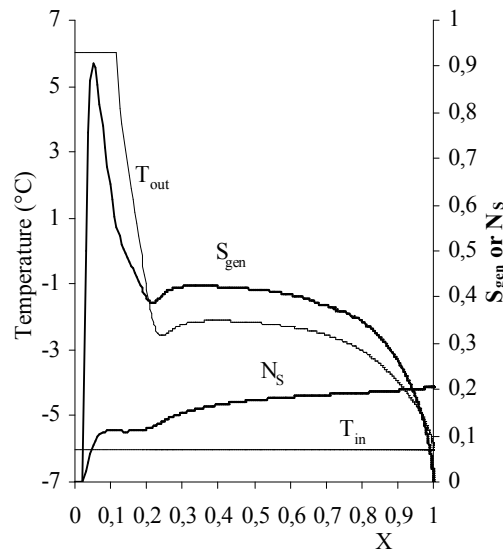


Figure 2. Results for a typical charge mode ($\Delta T_{in} = 6$ °C and $\tau = 750$ s).

On Figure 2, one can see the instantaneous rate of entropy \dot{S}_{gen} and the variation of the entropy generation number N_s versus X for a typical charge mode. To facilitate the interpretation, the variation of the outlet temperature T_{out} versus X is presented on the same figure.

Evolution of \dot{S}_{gen}

At the beginning of the charge process, the value of \dot{S}_{gen} is zero corresponding to the cooling of the fluid in the removable cover of the tank where there are no nodules. Afterwards, \dot{S}_{gen} increases rapidly because the heat transfer fluid enters the layer of nodules at a very different temperature from the initial temperature of the liquid PCM inside the nodules. Afterwards \dot{S}_{gen} decreases rapidly, then slowly, when some nod-

ules start to crystallize. \dot{S}_{gen} increases when most of the nodules are crystallizing. When a nodule begins to crystallize, the difference between the temperature of the transfer fluid and the PCM temperature inside the nodule increase sharply increasing \dot{S}_{gen} .

Evolution of N_S :

First before the cooled fluid reaches the nodules, corresponding to the values $X < 0.025$, the exergy destroyed is zero. Then N_S is increasing until the stored fluid has given way to the entering fluid i.e. when T_{out} begins to decrease quickly. Then N_S increases monotonically during the phase when the nodules crystallize. Except for the beginning of the cooling, this analysis shows that entropy generation due to crystallization of PCM is a major contributor to the total thermal irreversibilities.

On *Figure 3* and *Figure 4*, we can see that the fraction of destroyed exergy varies from about 10 % to 30 % , for a complete charge mode, according to the conditions of flow rate and inlet temperature. As expected, N_S increases as ΔT_{in} increases and τ decreases. We can observe that it is especially ΔT_{in} that has an influence on the variation of N_S .

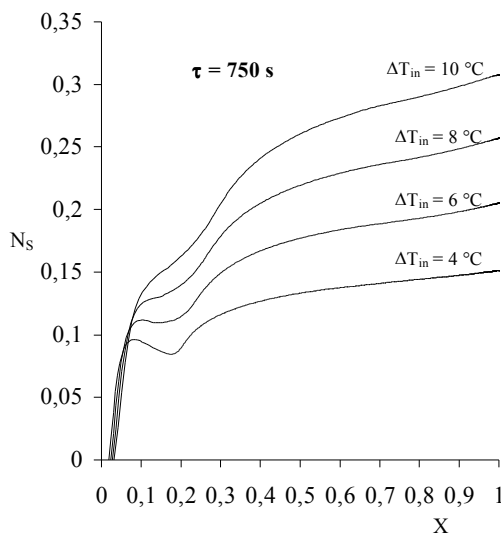


Figure 3. Fraction of destroyed exergy versus X for different ΔT_{in} .

It is important to notice that the duration of the storage does not enter directly into this simulation. In industrial conditions, the charge mode must be realised in a given time. Some previous studies (Bédécarrats et al., 1996) have shown the influence of the flow-rate and the final inlet temperature on the duration of the process. The duration of the charge mode is decreased when the

final inlet temperature is lowered and when the flow rate is increased. So, to complete a charge mode in a given duration, one can choose the appropriate couple flow-rate, final inlet temperature.

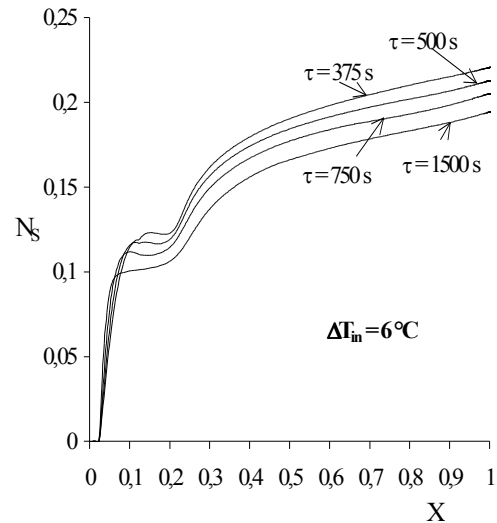


Figure 4. Fraction of destroyed exergy versus X for different τ .

So, practically, to minimise the irreversibility, it is better to choose a small ΔT_{in} (an inlet temperature near T_M) and a low value of τ (a high flow rate) instead of a big ΔT_{in} and a great value of τ , i.e. a low value of flow rate.

The three dimensional view offered by *Figure 5* shows the entropy generation number surface $N_S(\tau, \Delta T)$ for $X = 1$. One sees the variation of N_S versus ΔT_{in} and τ for a complete storage ($X = 1$). The curves formed by the entropy generation number surface with the plane for which N_S is constant are represented. We note that it is specially ΔT_{in} that has effect on the variation of N_S and that the influence of τ is more important when ΔT_{in} increases.

3.3.2 Influence of the undercooling.

Figure 6 shows the influence of the undercooling on the charge process.

One of the curves represents the variation of N_S without undercooling, i.e. one supposes that all the nodules begin to crystallize at the melting temperature T_M . This assumption is impossible because the undercooling cannot be cancelled. It is just an ideal case. Using different nucleation catalysts more or less effective, one can reduce ΔT . To represent the results, three values of undercooling were chosen : the normal undercooling corresponding to the minimum value ob-

tained experimentally ($\Delta T \approx 2.5$ °C), the medium undercooling corresponding to the normal undercooling lowered to $\Delta T \approx 4.0$ °C and the strong undercooling where $\Delta T \approx 5.5$ °C. It will be reminded that the crystallization phenomenon is stochastic. So the value of ΔT is an average value

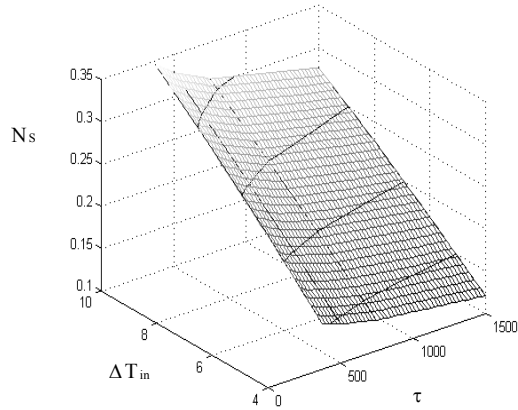


Figure 5. Entropy generation number versus ΔT_{in} and τ for $X = 1$.

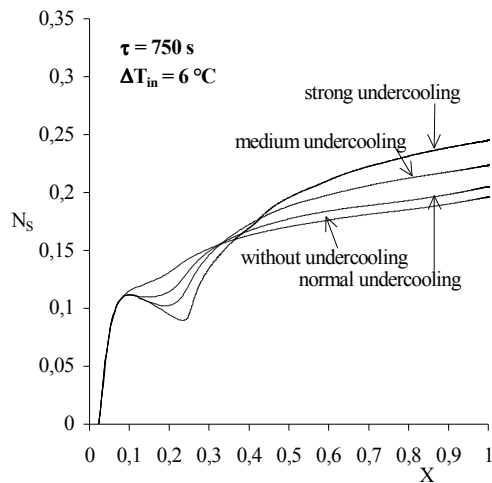


Figure 6. Influence of the undercooling

The fraction of destroyed exergy N_S is the same before the beginning of the crystallizations. When the crystallizations begin, N_S increases. The diminution of N_S between $X = 0.1$ and $X = 0.25$ corresponds to the delay of the crystallizations because of undercooling. More important the undercooling is, more important the diminution is. These results confirm that entropy generation due to crystallization of PCM is a major contributor to the total thermal irreversibilities. The principal result is that when the charge mode is complete, the fraction of destroyed exergy increases when the undercooling increases. This

result confirms the bad influence of the undercooling. So it is important to reduce the undercooling.

The study of a case where the undercooling is very important shows in Figure 7 the difficulties to interpret the second law perspectives. When the outlet temperature reaches the inlet temperature, no nodule has crystallized. This charge mode is only a sensible heat storage. The value of N_S is lower than in the case of a latent heat storage (Figure 6). However, the principal advantage in the use of phase change storage material is obviously the enhanced storage capacity compared with the same size of a system utilizing sensible heat storage material. On the basis of the second law evaluation, it does not appear that the system employing phase change storage material will always, or necessarily, be superior to that using a sensible heat storage material. The first law perspectives also must be considered.

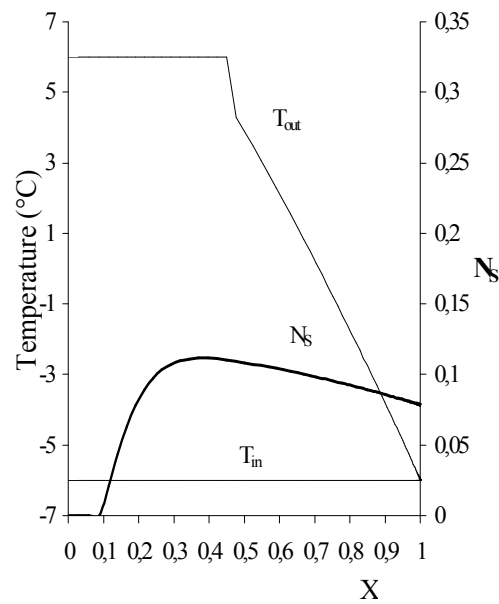


Figure 7. Results for a sensible charge mode ($\Delta T_{in} = 6$ °C and $\tau = 750$ s).

The three dimensional view offered by Figures 8, 9 and 10 shows the entropy generation number surface $N_S(\tau, \Delta T_{in})$ for $X = 1$ (a complete latent heat storage) for different values of the undercooling. One sees the variation of N_S versus ΔT_{in} and τ for a complete charge process ($X = 1$). The curves formed by the entropy generation number surface with the plane for which N_S is constant are represented.

For the case of a strong undercooling (Figure 10), the minimum value of ΔT_{in} to store the latent heat is 6°C.

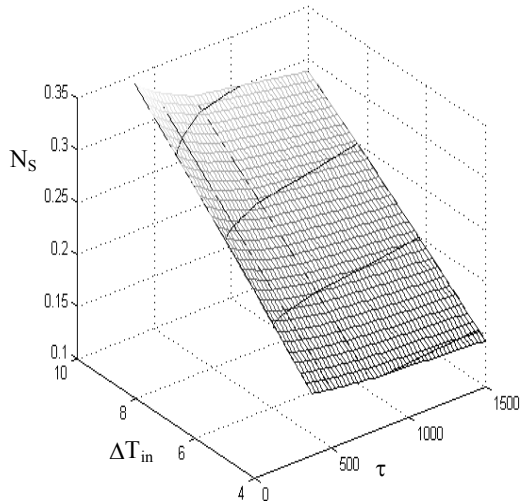


Figure 8. Entropy generation number versus ΔT_{in} and τ for $X = 1$ and without undercooling.

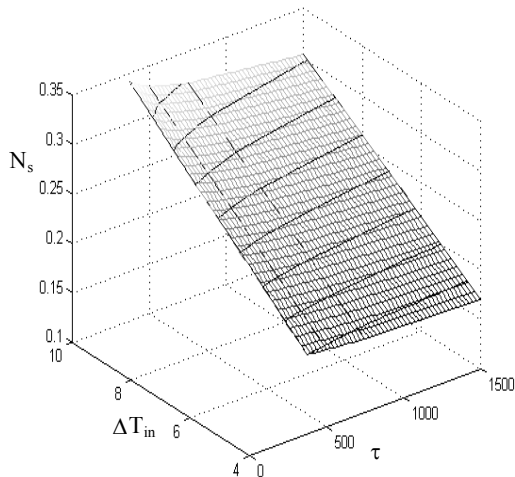


Figure 9. Entropy generation number versus ΔT_{in} and τ for $X = 1$ and a medium undercooling.

Whatever the value of the undercooling is, one can verify that N_s is more important when ΔT_{in} increases and when τ decreases. But one notes that the influence of ΔT_{in} and τ is less important when the undercooling is strong. One notes also the low influence of the undercooling when τ is low (375-500 s) and the strong influence when τ is high.

The stronger the undercooling is, the less influence τ has and the less influence ΔT_{in} has.

So, practically, to minimise the irreversibility, it is better to have a reduced undercooling and to choose a small ΔT_{in} instead of a great value of τ , i.e. a small value of flow rate. However, the inlet temperature T_{in} must be low enough to allow the crystallization of PCM.

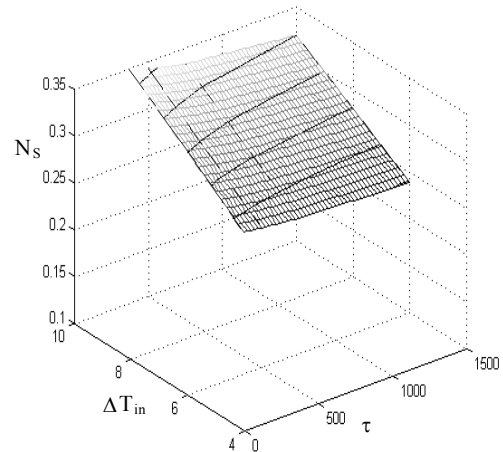


Figure 10. Entropy generation number versus ΔT_{in} and τ for $X = 1$ and a strong undercooling.

These results are interesting because they complete previous studies of the authors on phase-change energy storage. Experimental and numerical investigations (Bédécarrats et al. 1996, Dumas et al., 1994) showed the influence of the flow rate and the final inlet temperature on the charge mode. Here the different couples (flow rate, temperature) which permit to store the total energy in a given time are determined. It was impossible to conclude whether it is more efficient to choose a low flow-rate and a lower final inlet temperature rather than a greater flow rate and a higher final inlet temperature. This second law analysis appears a proper way to determine the best running of the charge mode : a big flow-rate and an inlet temperature near the melting temperature. However, the inlet temperature T_{in} must be low enough to allow the crystallization of PCM.

4. Conclusion

This paper presents a numerical analysis on the application of the second law of thermodynamics to a refrigeration phase-change storage in the case of the charge process. The entropy generation number N_s permits to evaluate the effects of the undercooling, the temperature difference and the flow rate, on the fraction of destroyed exergy.

The results confirm the detrimental influence of the undercooling. So, practically, to minimise the irreversibility, it is better to have a reduced undercooling and to choose a small ΔT_{in} and a low value of τ instead of a big ΔT_{in} and a great value of τ , i.e. a small value of flow rate.

Technologically, this result is extremely valuable because it guides the designer in the selection of the pumps and the refrigerating unit.

In practice, however, the cool thermal energy storage systems are operated in a cyclic manner, a single cycle consisting of a storage process is followed by a removal process (Strub and Bédécarrats, 1998). The future study will consider an entire operational cycle.

Nomenclature

c_{PCM}	specific heat of PCM
c_p	constant pressure specific heat of the fluid
$\dot{E}X_{cv}$	rate of exergy change of the control volume
h	heat transfer coefficient nodule – fluid
J	probability of crystallization of a nodule by unit time
k_S	effective thermal conductivity of solid PCM
k_p	thermal conductivity of nodule envelope
L_F	latent heat of melting of PCM
m_{PCM}	mass of PCM in a nodule
\dot{m}	mass flow rate of heat transfer fluid
M	number of layers
N	number of nodules in each layer
N_S	entropy generation number
$r_S(t)$	internal radius of solid PCM
r_e, r_i	outer and inner radius of nodule
s	specific entropy of the fluid
S	entropy
\dot{S}_{gen}	entropy generation rate
t	time
t_S	duration of an entire storage process
T_M	melting temperature of PCM
T	heat transfer fluid temperature
V	volume of the heat transfer fluid in a mesh
X	percentage of stored exergy

Greek letters

Δt	time step for the calculation
ΔT_{in}	difference between the inlet and the melting temperatures
ΔT	undercooling
ϕ_i	heat flux exchanged by the nodule i
$\theta(r,t)$	temperature of PCM.
ρ	density of heat transfer fluid
ρ_S	density of solid PCM
τ	time required for the fluid to flow through the tank

Subscripts

fluid	heat transfer fluid
i	nodule
in	inlet
j	refers to the number of a layer
out	outlet
PCM	Phase Change Material

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