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### ► To cite this version:

T. Dufour, J. Oignet, R. Ben Abdallah, Hong-Minh Hoang, Denis Leducq, et al.. Dynamic modelling of secondary refrigeration loop with co2 hydrate slurry. 11th IIR Conference on Phase Change Materials and Slurries for Refrigeration and Air Conditioning, May 2016, Karlsruhe, Germany. pp.8. hal-02605786

**HAL Id: hal-02605786**

**<https://hal.inrae.fr/hal-02605786>**

Submitted on 16 May 2020

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# DYNAMIC MODELLING OF SECONDARY REFRIGERATION LOOP WITH CO<sub>2</sub> HYDRATE SLURRY

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## ABSTRACT

Secondary refrigeration is an often used solution to reduce the amount of refrigerant leakage and the impact of refrigerants on global warming. The use of two-phase fluids in refrigeration systems is known to increase the quantity of stored energy. In this work, the impact of gas hydrates on the energy release of a heat exchanger is quantified thanks to the dynamic modelling of a secondary refrigeration system. The system is composed of a chiller, a stirred tank reactor (hydrate formation), a loop and a heat exchanger (hydrate dissociation). The model validated by experimental data can be used to simulate various operating conditions in transient and permanent regimes (various slurry mass flow rate, various thermodynamic conditions) and to compare their energy performances. The numerical and experimental results showed better heat exchanger efficiency with hydrate slurry than with water alone.

Keywords: hydrate slurry, CO<sub>2</sub>, heat transfer, modelling, thermal energy storage

## 1. INTRODUCTION

The development of cold production is a basic need in many fields but accounts for 8% of greenhouse gas (GHG) emissions, including the direct impact of primary refrigerants (principally HFC). Secondary refrigeration is used as a method to reduce primary refrigerant use (Fournaison *et al.* 2000) since it allows these refrigerants to be confined to machine rooms while carrying cold via an environment-friendly secondary fluid. In order to increase the storage capacity of the secondary fluid, phase change material slurries can be used such as ice, paraffin, or hydrate slurries (Koh *et al.* 2012; Zhang *et al.* 2012). Hydrates are ice-like crystals able to trap gas molecules (Sloan 1998; Sloan *et al.* 2008). They are stable over a wide range of temperature (253-313 K) and can thus be used as phase change materials (PCM) in cold storage applications (Mao *et al.* 2007). Moreover, by dispersing hydrate crystals in liquid phase, it is possible to form slurries with relatively low viscosity capable of carrying cold in secondary loops (Delahaye *et al.* 2008; Jerbi *et al.* 2013; Youssef *et al.* 2013).

CO<sub>2</sub> hydrate is particularly interesting for energy storage since it is the PCM with the highest latent heat of melting (374 kJ.kg<sup>-1</sup><sub>hyd</sub>, at P > 1 MPa) at normal temperatures for air conditioning (Fournaison *et al.* 2004; Marinhas *et al.* 2006). However, the capacity of hydrates to restore energy during the dissociation process (in term of quantity and heat flow rate) has yet to be determined. This capacity is highly important if hydrate is considered for applications in refrigeration and air conditioning. The aim of this article is to study hydrate slurry behavior in a heat exchanger using experimental investigations and modelling development. The experimental study was carried out on an experimental set up in which hydrates were formed in a stirred tank reactor and then transported to the heat exchanger using a circulation loop. A numerical study was also carried out in which the heat exchanger was modelled using a finite volume method. The model which was validated using experimental data allows the impact of hydrates on the system efficiency to be predicted.

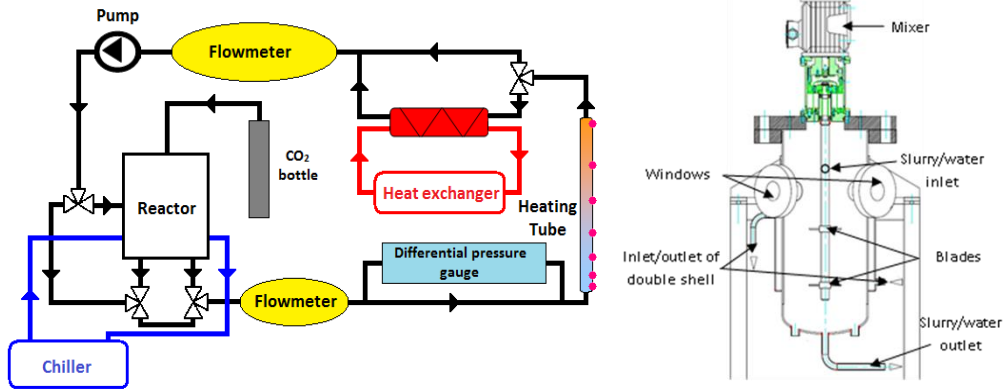
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## 2. MATERIAL AND METHODS

### 2.1. Experimental setup: pilot loop and heat exchanger

In order to study the use of CO<sub>2</sub> hydrate slurry, a pilot loop (Figure 1a) has been developed (Jerbi *et al.* 2010; Jerbi *et al.* 2013). This loop can be divided into three parts: a tank reactor (Figure 1b) where hydrates were formed according to the protocol described in Jerbi *et al.* 2013, a circulation loop, and a heat exchanger where hydrates are dissociated using a hot fluid.



a. Pilot loop

b. Tank reactor

Figure 1: Pilot loop and tank schemes The heat exchanger (Figure 2a) is composed of a helical copper pipe in a cylindrical stainless steel vessel. Hydrate slurry flows inside the pipe (internal diameter of 7.74 mm, external diameter of 9.5 mm, with a capacity of 470 mL) which is connected to the circulation loop. A hot fluid flows inside this vessel (internal diameter of 21 cm, external diameter of 25 cm and an internal volume of 27 l).

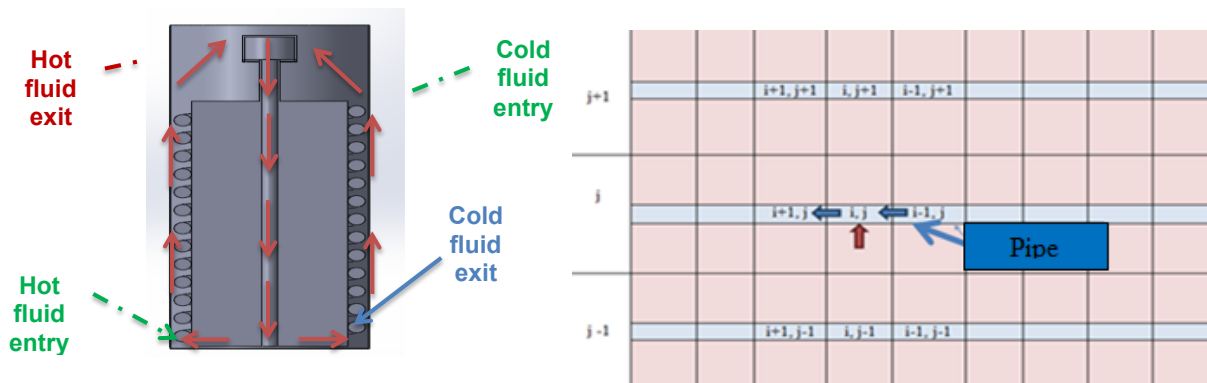


Figure 2: a) Heat exchanger scheme

b) segmentation of the heat exchanger

The hot side is connected to a Vulcatherm (type 10805) having a heating capacity of 6 kW. The heat exchanger is instrumented by four calibrated thermocouples ( $\pm 0.3$  K) at the inlet and outlet of the hot and cold fluids.

### 2.2. Heat exchanger modelling

#### 2.2.1. Heat balance

A model was developed to simulate the restitution of energy stored by hydrates in a heat exchanger. The heat exchanger's pipe composed of several coils is segmented according to two directions: horizontal (index  $i$ , along each coil) and vertical (index  $j$ ) as shown in Figure 2b. Firstly the heat transfer between the cold and hot fluids and the walls was modeled following the finite volume method. Hot fluid, which flows around the

helical pipe, is supposed to be at the same temperature along each coil which corresponds to one vertical j position. According to that assumption, equation (1) is used to evaluate hot fluid temperature:

$$m_h C_{p,h} \frac{dT_{h,j}}{dt} = \dot{m}_h C_{p,h} (T_{h,j-1} - T_{h,j+1}) + h_h S_{wh} \left( \frac{(T_{h,j+1} - T_{h,j-1})}{\ln\left(\frac{(T_{h,j+1} - T_{p,j})}{(T_{h,j-1} - T_{p,j})}\right)} \right) \quad (1)$$

Cold fluid temperature is calculated at each cell (i,j):

$$m_c C_{p,c} \frac{dT_{c,ij}}{dt} = \dot{m}_c C_{p,c} (T_{c,i-1j} - T_{c,i+1j}) + h_c S_{wc} \left( \frac{(T_{c,i+1j} - T_{c,i-1j})}{\ln\left(\frac{(T_{c,i+1j} - T_{p,ij})}{(T_{c,i-1j} - T_{p,ij})}\right)} \right) \quad (2)$$

Finally, wall temperature is determined thanks to the heat balance with hot and cold fluids:

$$m_p C_p \frac{dT_{p,j}}{dt} = -h_h S_{wh} \left( \frac{(T_{h,j+1} - T_{h,j-1})}{\ln\left(\frac{(T_{h,j+1} - T_{p,ij})}{(T_{h,j-1} - T_{p,ij})}\right)} \right) - \sum_i h_c S_{wc} \left( \frac{(T_{c,i+1j} - T_{c,i-1j})}{\ln\left(\frac{(T_{c,i+1j} - T_{p,ij})}{(T_{c,i-1j} - T_{p,ij})}\right)} \right) \quad (3)$$

This non-linear system is resolved under an implicit scheme.

### 2.2.2. Evaluation of hydrate quantity

The aim of this model is to simulate and evaluate CO<sub>2</sub> hydrate behavior in a heat exchanger. To achieve this goal, the impact of the latent heat of hydrates has to be considered. Firstly, the amount of CO<sub>2</sub> hydrates is evaluated thanks to a CO<sub>2</sub> mass balance. Indeed, the amount of CO<sub>2</sub> present in the system can be found in three phases: vapour, dissolved liquid, and CO<sub>2</sub> trapped in hydrate. This mass balance, expressed by the correlation developed by (Marinhas et al. 2006), was used to quantify CO<sub>2</sub> hydrates in the system thanks to equation (4) (4):

$$n_h = \frac{n_{CO_2, tot} - \sigma_{CO_2} \frac{\rho_{H_2O} V_l}{M_{H_2O}} - \left( \frac{P_{CO_2}}{Z(P_{CO_2}, T)TR} \right) (V_{tot} - (n_{H_2O,l} - nb_h n_h) (M_{H_2O} + \sigma_{CO_2} M_{CO_2}))}{1 - \sigma_{CO_2} nb_h + \left( \frac{P_{CO_2}}{Z(P_{CO_2}, T)TR} \right) ((nb_h n_h) (M_{H_2O} + \sigma_{CO_2} M_{CO_2}) - \frac{M_h}{\rho_h})} \quad (4)$$

### 2.2.3. Apparent heat capacity

Hydrate dissociation (phase change) in the heat exchanger is considered using the apparent heat capacity method (C<sub>p,c</sub>). At each cell, the amount of dissociated hydrate is calculated (Cf. 2.2.2). The dissociation kinetics is not taken into account in a first approach: hydrate dissociation is supposed to be achieved at the equilibrium (L<sub>w</sub>-H-V, Figure 3 Figure 3). Then, the apparent heat capacity of hydrate slurry is evaluated (eq. (5) (5)) and placed in eq. (2).

$$C_{p-ap}(T) = \frac{\Delta H d\phi + C_{p,L}(1-\phi)dT + C_{p,s}\phi dT}{dT} \quad (5)$$

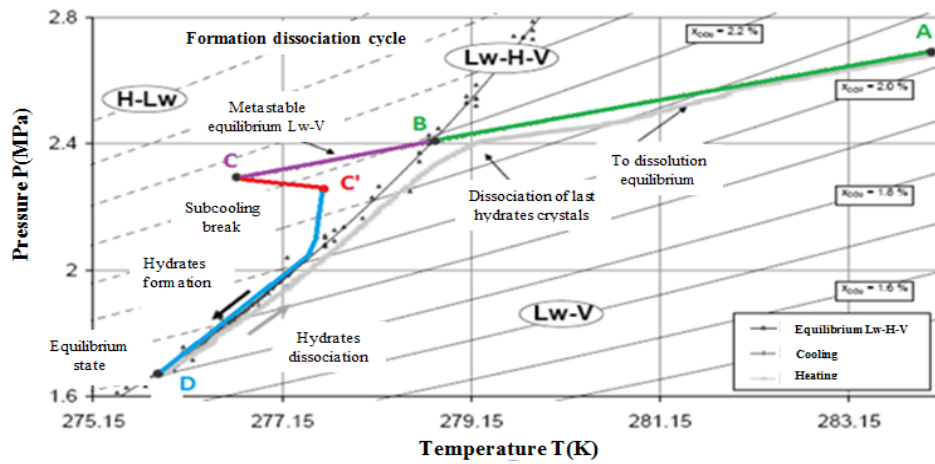


Figure 3: CO<sub>2</sub>-water phase diagram

### 2.3. Evaluation of hydrates dissociation energy

In order to evaluate the role of gas hydrates, heat transfer contribution is divided into sensible and latent heat:

$$\dot{Q}_s = (\dot{m}_h C_{p,h} \Delta T + \dot{m}_l C_{p,l} \Delta T) \quad (6)$$

$$\dot{Q}_h = d \dot{m}_h \Delta H \quad (7)$$

The efficiency of the heat exchanger, which is the ratio of the heat exchange between hot and cold fluids divided by the maximum amount of heat exchangeable, is evaluated thanks to equation (8)-(8).

$$\varepsilon = \frac{\dot{m} C_p (T_{in} - T_{out})}{(\dot{m} C_p)_{\min} (T_{h,in} - T_{c,in})} \quad (8)$$

By convention, the term  $\dot{m} C_p$  in the numerator and in the denominator chosen in equation (8)-(8) is always the hot side (water).

## 3. RESULTS AND DISCUSSION

In this section, the heat exchanger model is firstly validated on water and CO<sub>2</sub> hydrate systems. Secondly, results on energy restitution using CO<sub>2</sub> hydrate slurry, are shown. The improvement brought by hydrate slurry and an evaluation of the latent and sensible heat transfer rates are also presented.

### 3.1. Model validation

The model described above was validated using experimental data obtained with water and hydrate slurries as cold fluids. Figure 4 shows the comparison between experimental and numerical results for water. The green dot curves represent experimental inlet temperature for hot and cold fluids, which are used as input data for the model. The results of outlet temperature (cold and hot) calculated by the model are in good agreement with experiment data that has an average error of 0.1 K. Most of the error is found at the beginning of the experiment, due to hot fluid inertia at the beginning of the heating process.

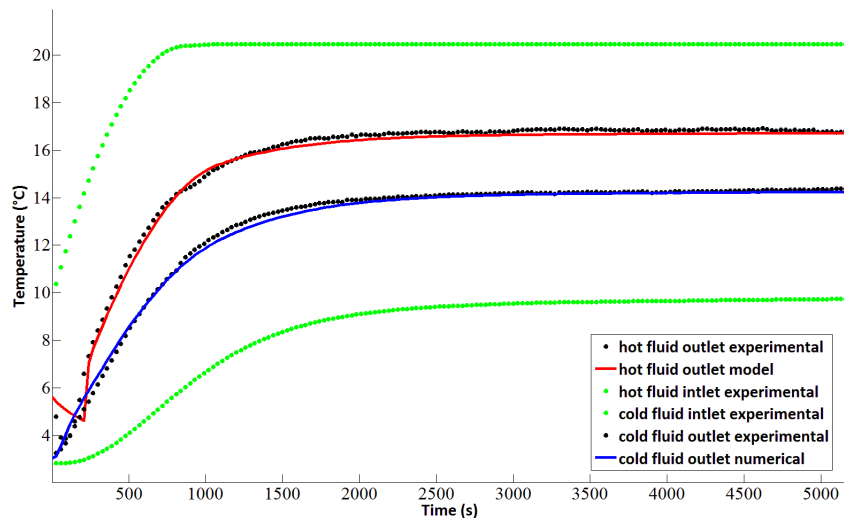


Figure 4: Model validation on water

A comparison with hydrate slurry was also achieved (Figure 5) in order to validate the apparent capacity approach. Although the model seems to be less accurate than with water, the main error is due to hot fluid. Nevertheless, temperature evolution is still in good agreement with experiments (average error of 0.3K).

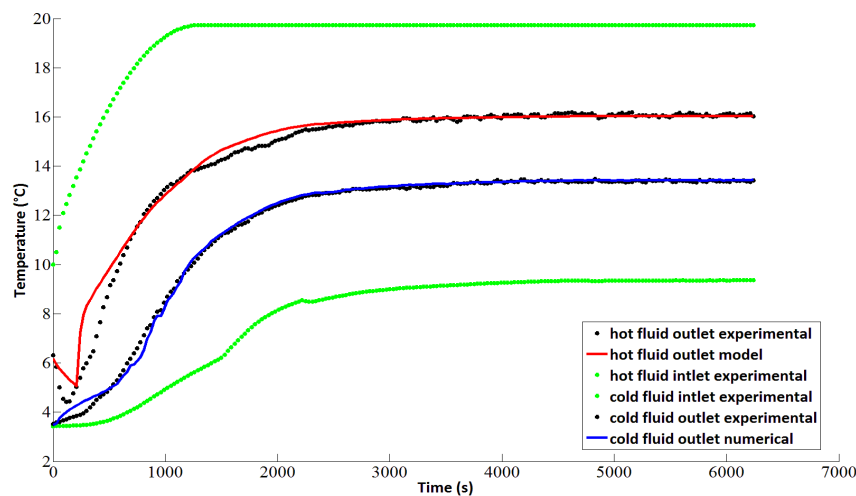
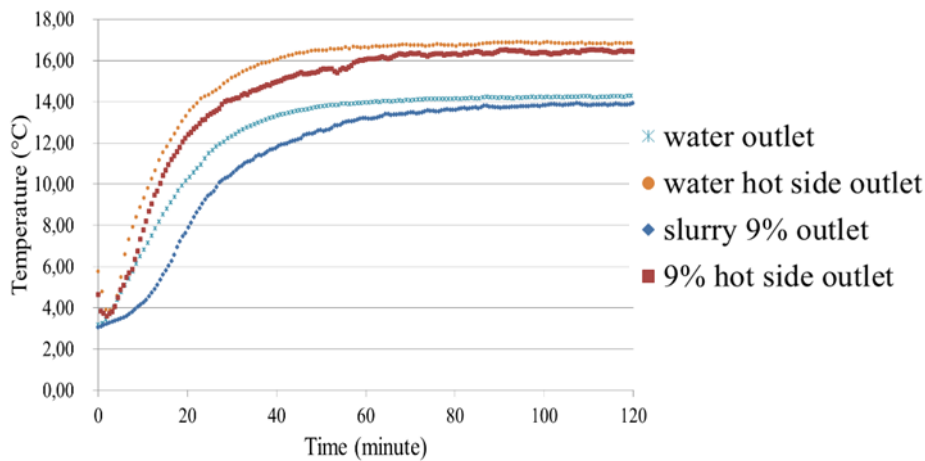


Figure 5: Model validation on hydrate slurry

### 3.2. Impact of CO<sub>2</sub> hydrates slurry on system efficiency

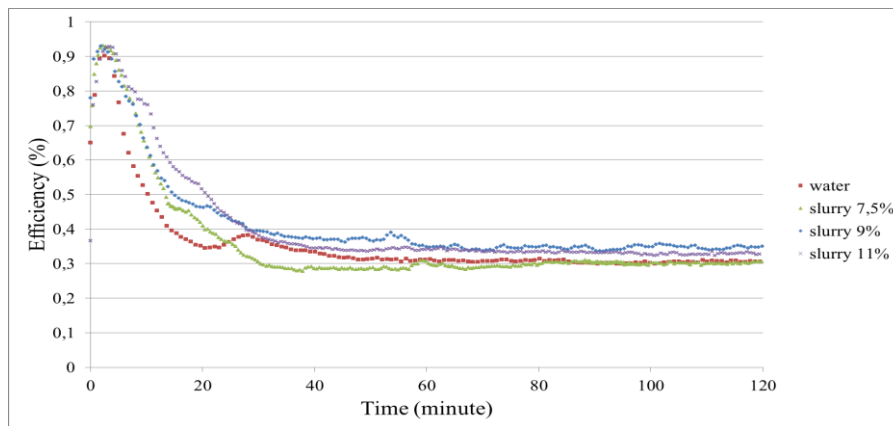
In order to evaluate the impact of slurry on the heat exchanger, slurry with different mass fractions was formed and circulated in the loop until the heat exchanger in which slurry was heated. The heating protocol was the same for water and hydrate slurry: same set point temperature (20°C) and same flow rate for the hot fluid. Figure 6 shows the evolution of outlet temperatures (cold and hot, with and without hydrate). Temperature evolution depends on the presence or not of hydrate in the fluid: outlet temperatures with hydrates are lower than those with water. Indeed, the presence of hydrates increases thermal inertia (by latent

heat) and thus stabilizes the slurry towards low temperatures. As a consequence, the time of restitution (the time during which the stationary regime is not attained) is increased.



**Figure 6: Outlet temperature of cold and hot side for various mass fractions**

This thermal improvement is characterized by heat exchanger efficiency presented in [Figure 7](#)~~Figure 8~~. The curves show that a higher mass fraction provides a higher efficiency and for a longer time. As pointed out previously, this improvement is due to the latent heat of hydrates which stabilizes cold fluid temperature, which maintains a higher temperature difference with the hot fluid.



**Figure 7: Efficiency of the heat exchanger for various mass fractions**

The contributions of sensible and latent heat are presented in [Figure 8](#)~~Figure 9~~ for water and hydrate slurry. Firstly it is noticeable that the total thermal power is higher for hydrate slurry (dark curve) than for water (blue curve). This result confirms the improvement brought by latent heat. Secondly, in the case of hydrate slurry, the latent heat due to hydrate melting contributes mainly in the heat exchange during the first step (from 0 to approximately 27 min, cross of green and red curve). Consequently, the sensible heat of hydrate slurry contributes more lately to the heat exchange. This thermal behavior in two steps (first latent, then sensible) may explain the thermal stabilization and efficiency increase due to hydrates described previously.

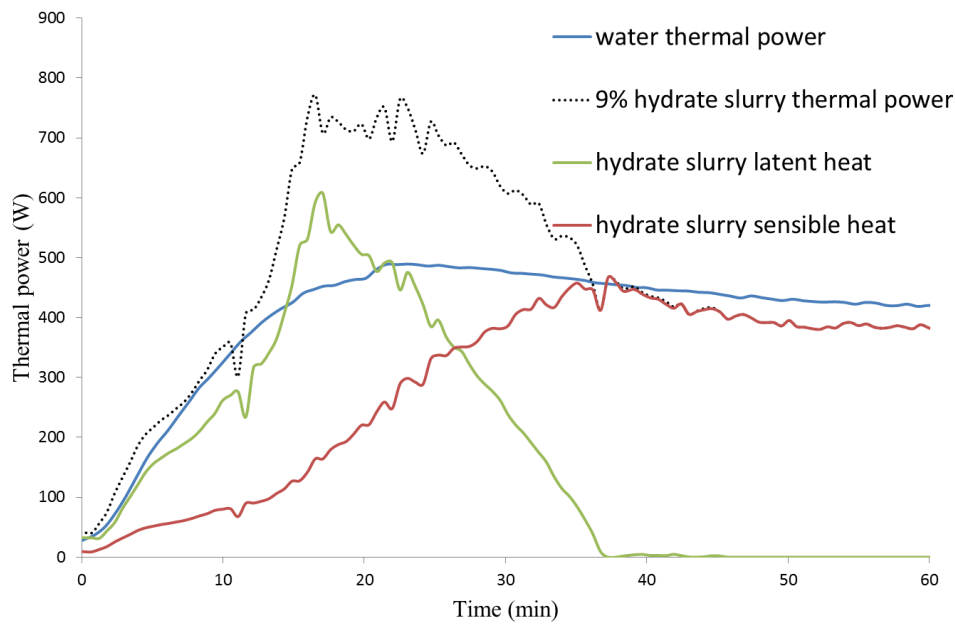


Figure 89: Different contribution of sensible and latent heat during energy restitution and comparison with water

## 4. CONCLUSION

In the current study, the impact of hydrates on the performance of a heat exchanger has been considered. First, the presence of hydrates improves the amount of restituted energy, which is a known result related to energy density of any slurry compared to liquid systems. Consequently, the time of energy restitution is longer with hydrates than with water, and it is even longer when the fraction is higher. In addition, the total thermal power is higher with hydrate slurry than with water, which shows the ability to increase heat transfer. Moreover, the latent heat of hydrate slurry contributes mainly in the heat exchange during the first step, and the sensible heat contributes to the heat exchange at a later stage. This thermal behavior can explain the thermal stabilization of the system. Consequently, the use of hydrate slurry can improve both thermal energy and power restitution.

Besides, the model developed for this work is able to approximate hydrate dissociation by an apparent heat capacity in order to compute the use of hydrates in a heat exchanger. This kind of approximation allows a full system modeling using hydrate slurry.

## NOMENCLATURE

$m$	weight, kg	$Q$	energy, J		<i>Subscripts</i>
$C_p$	specific heat, $J.kg^{-1}.K^{-1}$	$\Delta H$	phase change enthalpy, $J.kg^{-1}$	$l$	liquid
$T$	temperature, K		<i>Greeks symbols</i>	$h$	hydrate
$x$	TBPB mass fraction	$\varphi$	hydrates mass fraction	$w$	water
$nbh$	hydratation number	$\phi$	flux, W	$c$	stoichiometric
$t$	time, s	$\sigma$	solubility	$In$	entering heat exchanger
$\dot{m}$	Mass flow rate ( $kg.s^{-1}$ )			$Out$	exiting heat exchanger

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