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# ENERGY STUDY OF CO<sub>2</sub> HYDRATE SLURRIES FORMATION IN A TANK REACTOR

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## ABSTRACT

The work performed at Irstea investigates the use of CO<sub>2</sub> hydrates slurries as phase change materials. A tank with a pilot loop is used to form slurries by subcooling. Several studies (thermal, rheological) were carried out to evaluate slurries characteristics useful for a complete energy study of the system. The aim of this paper is to present the modelling of a device for hydrate slurries formation including a tank reactor and a loop. Finite volume method with implicit time discretization scheme is used. This model allows predicting the slurry temperature evolution; it is validated by experimental data on a hydrate formation during a cooling process. The energy balance is performed to evaluate the storage efficiency and the heat losses through the reactor wall.

## NOMENCLATURE

$m$	weight, $kg$	<i>Greeks symbols</i>
$C_p$	specific heat, $J.kg^{-1}.K^{-1}$	$\eta$ efficiency
$T$	temperature, $K$	$\phi$ flux, $W$
$t$	tims, $s$	<i>Subscripts</i>
$Q$	energy, $J$	$l$ liquid
$H$	Energy density, $kJ.kg^{-1}.K^{-1}$	$h$ hydrate

## 1. INTRODUCTION

Nowadays, cold production has an important impact on the environment. 80 % of the pollution caused by cold production is due to the energy consumption of the installations and 20 % are caused by the leakage of the refrigerant gas. The classical refrigerant fluids that are used for cold production are HCFC, HFC and CFC. These fluids have a bad impact on the environment and after Montreal and Kyoto protocols their use has been extremely limited and even forbidden. That's why it becomes important to find new way to produce and transport cold energy. The secondary refrigeration could be a solution to reduce the use of primary refrigerant fluids (Fournaison and Guilpart, 2000). The main advantage of this system is to reduce the need of primary refrigerant fluids. The cold production is still carried out by classical refrigerant fluid in a smaller loop but the cold storage and transport is now carried out by a second fluid neutral to the environment (water) in a second loop which has bigger dimensions. In order to increase the storage capacity of the second fluid, phase change materials can be used such as CO<sub>2</sub> hydrate slurries (Koh *et al.*, 2012). Hydrates are solid particles able to trap gas molecules (Sloan, 1998; Sloan and Koh, 2008). They are formed at positives temperatures and high pressures (Mao *et al.*, 2007). The energy is stored mainly during a phase change process by latent heat (Zhang and Ma, 2012). Actually, they have high density energy ( $374 kJ.kg^{-1}_{hyd}$ ) (Marinhas *et al.*, 2006) higher than that of ice ( $333 kJ.kg^{-1}$ ) which make them very interesting for cold storage (Fournaison *et al.*, 2004). These solid particles are then used in a carrier fluid such as water to transport the cold energy to the place of use. Some studies performed at Irstea (Youssef *et al.*, 2009; Delahaye *et al.*, 2011) have shown the important role of hydrate slurries in the field of refrigeration (Delahaye *et al.*, 2008) The aim of the present paper is to introduce a modelling of a tank for hydrate formation and a secondary loop. To carry out this model a finite volume method has been used on the reactor

and a heat flux balance was applied on each node of the mesh with an implicit discretization scheme. This model enables to carry out an energetic balance on the tank/loop system and evaluate the storage efficiency of the hydrates slurries. The first results have shown that the nodal model is in good agreement with the experimental data. Furthermore the total storage efficiency (stored/input energy) is ~ 50 % while the hydrate storage efficiency (latent stored//input energy) is ~ 40 % for a slurry with 22 % vol.

## 2. EXPERIMENTAL MATERIAL

In order to study the CO<sub>2</sub> hydrate slurry, a pilot loop is set up (Jerbi *et al.*, 2010; Jerbi *et al.*, 2013). This loop can be divided in two parts. The first one is the reactor used to form the slurry by a global cooling of the vessel. The second one is the loop for the circulation of the flow.

### 2.1. Formation tank

The stainless steel reactor has a diameter of 273 mm and a height of 495 mm with a wall thickness of 5 mm. It has a volume of 26.4 l and an operating pressure limited to 3.5 MPa (Fig.1). One inlet port and two outlet ports are present to permit the slurry flow in the loop. Two glass windows are also present in order to observe the formation of hydrate slurry on the gas-liquid interface. The reactor has a jacket for the circulation of the refrigerating fluid coming from the chiller. Thus, hydrates can be formed by tank cooling. The whole reactor is covered by an insulating layer to avoid thermal losses by the wall. Furthermore, a mixer is used to increase the rate of CO<sub>2</sub> hydrate slurry formation, by breaking hydrate barrier or crust which can form at the gas-liquid interface and prevent gas propagation into water during hydrate formation. The tank reactor is shown on Figure 1:

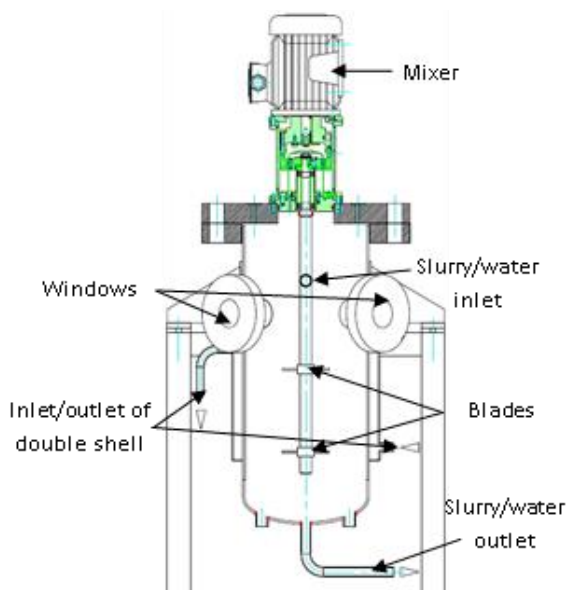


Figure 1: Tank scheme

### 2.2. Pilot loop

The experimental loop is composed of stainless pipes with an internal diameter of 7.74 mm and an external diameter of 9.52 mm. The inner volume of the loop is determined at 0.75 l. The experimental loop is equipped with a 220 type Axflow Micro Pump (adjustable speed, differential pressure of 0.4 MPa static pressure of 10 MPa, flow rate pump max of 200 l.h<sup>-1</sup>). The flow rate is measured by an Emerson CMF050 Coriolis Flow and Density Meters with two parallel tubes of measurement. This flowmeter is placed at the outlet of the tank to measure the mass flow, the density and the temperature of the CO<sub>2</sub> hydrate slurries. A differential pressure gauge is placed on a linear part of the circuit to measure pressure drops generated by the displacement of the slurry. The device is also equipped with eight PT 100 located at various positions and two pressure gauges. Finally, the whole system (tank reactor + loop) is placed in a temperature controlled cold room.

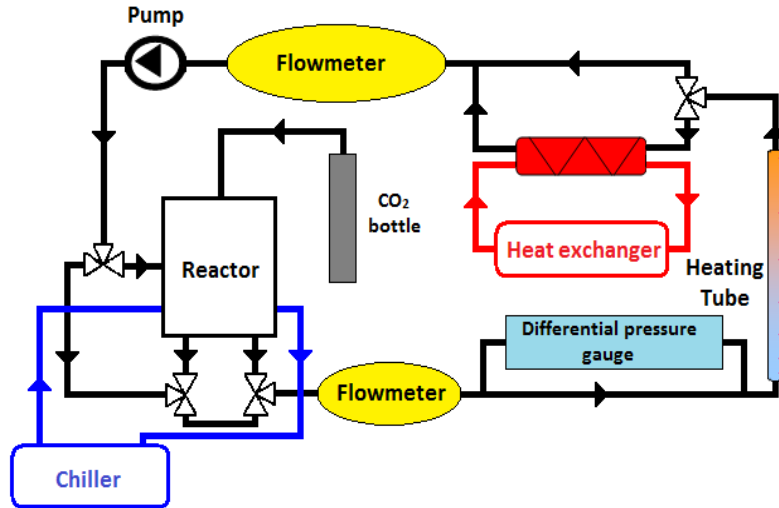


Figure 2 : Pilot loop scheme

### 3. NUMERICAL METHODS

In order to evaluate the total energy stored within the tank, a pseudo-homogeneous model was written. This model is able to estimate temperature evolution in the reactor and hydrate formation rate. This model is based on a heat flux balance and a CO<sub>2</sub> balance inside the tank.

#### 3.1. Thermal transfer modelling

The tank has been modelled following the finite volume method in order to predict the thermal exchange. The inside of the reactor was divided in six parts from the bottom to the top in order to simulate different rate of filling. The tank wall doesn't have large temperature variations, thus temperature walls is considered radially constant. Figure 3 gives a representation of the tank segmentation.

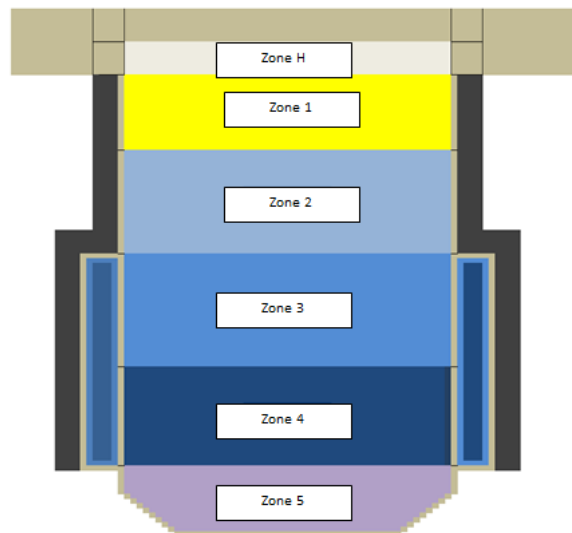


Figure 3 : Representation of the tank and its different parts

A Thermal exchange balance is applied on each node (zones and walls) of the tank:

$$mC_p \frac{dT}{dt} = \sum \phi_{cond} + \sum \phi_{conv} \quad (1)$$

This balance assumes that the heat exchange is only due to conductive or convective flux. It is applied on all the nodes of the system and allows getting a matrix with N equations to N unknown. A system implicit resolution has been chosen to improve the model convergence. The grid (zones) and the model were checked by several tries on water temperature evolution inside the reactor without phase change. Moreover, in the presence of hydrate slurries, it is necessary to include hydrate formation rate in the model, as a source term.

### 3.2. Stored energy and efficiency modelling

Solid particles rate can be quantify by a CO<sub>2</sub> balance carry out on the tank (Marinhas *et al.*, 2007) through its different phases (vapour, liquid, hydrate). The temperature evolution modelling takes into account the heat released during the hydrate formation process. The stored energy in the tank is determined by an integrated calculation on the instant power equation stored in the system, as we can see on the following relation:

$$Q_{stored} = \int \left( \frac{m_l C_{p_l} \Delta T}{dt} + \frac{m_h C_{p_h} \Delta T}{dt} + \frac{dm_h \Delta H}{dt} \right) dt \quad (2)$$

The previous equation can be divided in two parts. The first one concerns the stored energy by hydrates with latent and sensible heat and the second one is about the stored energy by water remaining at liquid state which is represented by the two following equation:

$$Q_{hyd} = \int \left( \frac{m_h C_{p_h} \Delta T}{dt} + \frac{dm_h \Delta H}{dt} \right) dt \quad (3)$$

$$Q_{liq} = \int \left( \frac{m_l C_{p_l} \Delta T}{dt} \right) dt \quad (4)$$

By the knowledge of the energy coming from the chiller to the tank through the jacket, it becomes possible to evaluate a “global efficiency” of the experimental device. This efficiency is determined by dividing the total stored energy in the system with the energy given par the chiller.

$$\eta_{system} = \frac{Q_{stored}}{Q_{chiller}} = \frac{Q_{chiller} - Q_{losses}}{Q_{chiller}} \quad (5)$$

This global efficiency characterised the useful energy. It can be compared to “hydrate formation efficiency”, which is determined by dividing the energy required to the hydrates formation with the energy given by the chiller.

$$\eta_{formation} = \frac{Q_{hyd}}{Q_{chiller}} \quad (6)$$

A third ratio is also determined in order to evaluate the importance of the heat storage capacity of the hydrates with the energy stored by water with sensible heat. This “hydrate slurry ratio” is estimated by dividing the two previous energies.

$$\eta_{hyd\ storage} = \frac{Q_{hyd}}{Q_{stored}} = \frac{Q_{hyd}}{Q_{hyd} + Q_{liq}} \quad (7)$$

## 4. RESULTS AND DISCUSS

The aim of this section is to present the first results on the energetic study and the tank modelling. Calculations on stored energies, efficiencies and predicting temperature evolution system are shown. These results allowed the global efficiency of the system to be assessed, but also hydrate formation efficiency and hydrate slurry ratio. Firstly, the energy model is checked on water, then on hydrate slurries.

### 4.1. Water model validation

The model was firstly applied on a non-stirred tank with water and on a stirred tank with water, in order to observe the ability of the model to take into account the agitation of the system without phase change. For this purpose, experiments were carried out on the tank reactor: the water inside the tank was cooled by the chiller with and without stirring. Then the temperature evolution between the experimental data and the evolution predicted by the model were compared. The results are shown on the following figures.

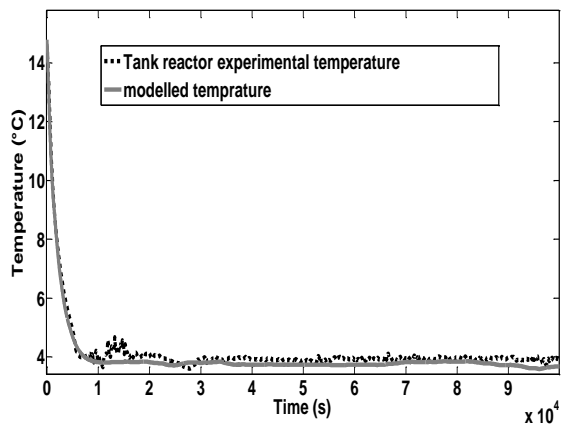


Figure 4: Water system without stirring

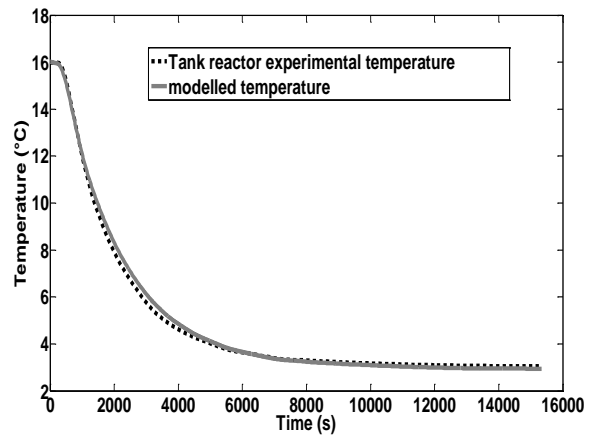


Figure 5: Water system with stirring

The previous figures represent the water temperature evolution inside the storage tank in terms of time for two different tries: with and without reactor stirring. The model is able to take into account the stirring phenomenon due to a convective heat transfer coefficient variation inside the tank. The main observation is about the low gap ( $0.1^{\circ}\text{C}$ ) between the experimental data and the numerical model. It means that the model is good enough to represent the temperature data inside the reactor and the thermal behaviour of a single phase fluid. Another observation can be made concerning the system cooling which is faster when the stirring is activated. It can be explained by a better homogenization of the system temperature due to the slurry mashing. Nevertheless, the stirring has an impact only on the speed cooling, the final temperature system remaining the same.

#### 4.2. $\text{CO}_2$ hydrate slurries temperature evolution modelling

As previously described, hydrate slurry modelling required an hydrate formation modelling in the aqueous phase in addition to the thermal transfer and convective heat transfer coefficient evaluation and also a pressure evaluation in the system. In order to verify this approach, the program was tried on hydrate slurries experimental data between 10 and 20% of volume solid fraction as shown on the following figures:

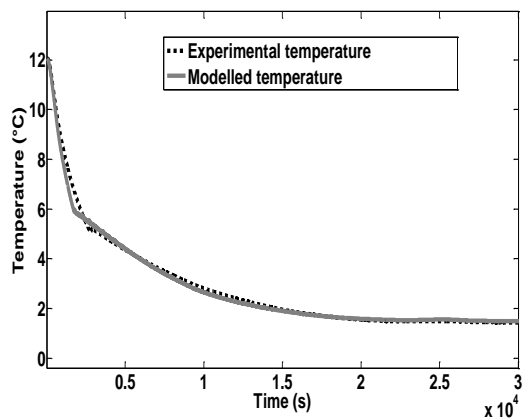


Figure 6: Hydrate slurry with 14% vol

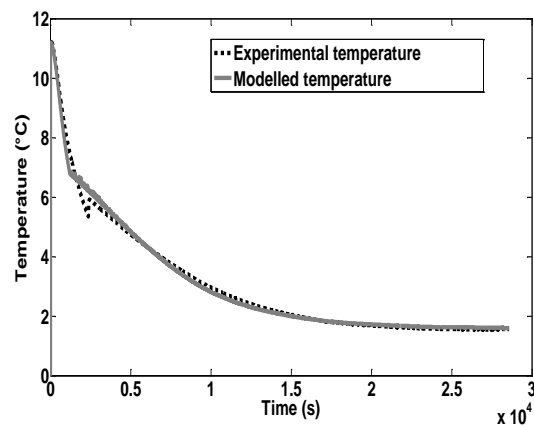


Figure 7: Hydrate slurry with 18% vol

The previous figures represent the numerical and experimental curves for water- $\text{CO}_2$  system temperature evolution leading to the hydrate formation with solid fractions between 14 and 18%. Whereas the temperature gap between experimental and numerical data is low ( $0.2^{\circ}\text{C}$ ), the curves are slightly distant in the area following the hydrate formation. This phenomenon can be explained by the model hypothesis. Indeed, the program neglects the subcooling break leading to the hydrate formation. In the model, hydrates are considered to be formed when temperature and pressure data reach hydrate-liquid-vapor equilibrium curve on the phase diagram. Consequently, the gap between experimental and modelled data disappears when the system is near from the thermodynamic balance. In this condition, the model is relevant to represent the hydrate slurry temperature evolution. These results allow storage efficiency to be estimated.

### 4.3. Storage efficiency determination

Due to the temperature evolution previously presented, it is possible to evaluate efficiencies related the energy stored in the tank or to hydrates formation. A study of the thermal losses through the tank walls and of the whole system efficiency was also carried out. The following Table 1 represents the efficiencies previously described for many solid fractions from water to 20% vol.

Table 1: Several efficiencies for different solid fraction hydrate slurries

Fraction	Global efficiency	formation efficiency	storage efficiency
0 %	38 %	0 %	0 %
11.1%	47 %	22 %	47 %
13.3%	47 %	27 %	57 %
14%	46 %	25 %	54 %
15.8%	51 %	29 %	57 %
16.8%	48 %	28 %	59 %
17.6%	45 %	31 %	69 %
18.5%	48 %	31 %	64 %
19.7%	49 %	35 %	71 %
20.1%	61 %	45 %	73 %
21.5%	45 %	34 %	75 %
22.15%	48 %	37 %	77 %

The storage efficiency increases with the solid fraction which is an expected result because this efficiency represents the energy rate stored in the slurry by latent and sensible heat. Nevertheless the two others efficiencies take into account the thermal losses to the environment, explaining why the other data are less ordered. It is also important to have a good representation of energy distribution (provided, stored, lost) in the system. The system energy balance is then represented on the following Figure 8. The comparison between provided, stored and lost energy can be observed.

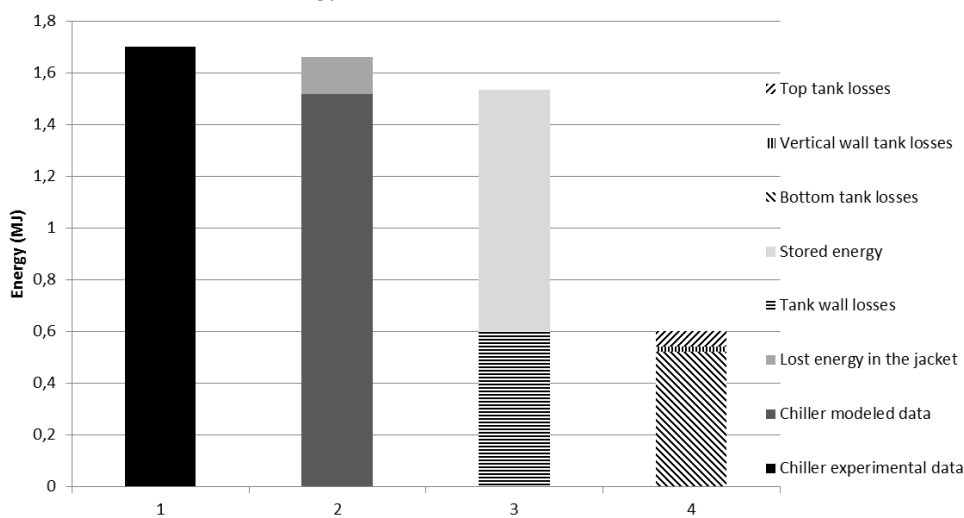


Figure 8: Representation of the energy distribution inside the tank

On the previous Figure 8, the first drawbar shows the whole energy given to the system by the chiller, calculated with the experimental data. The second drawbar is the energy transferred to the tank by the walls and the energy lost by the jacket calculated with the model. The comparison between the height of the two first drawbars shows that they are very close (the gap is less than 2%), which validate the model in a first approach. The third drawbar represents the stored energy (latent and sensible heat) in the tank and the losses to the walls. The last one shows energy loss repartition through the different tank walls. This study was carried out on the reactor but it could be interesting to include the loop and observe its impact on the storage and losses. Then, the following Figure 9 shows the amount of energy stored in the system (tank and loop)

given by the chiller, and represent how this energy is distributed in the system (latent storage, sensible storage and losses through the walls).

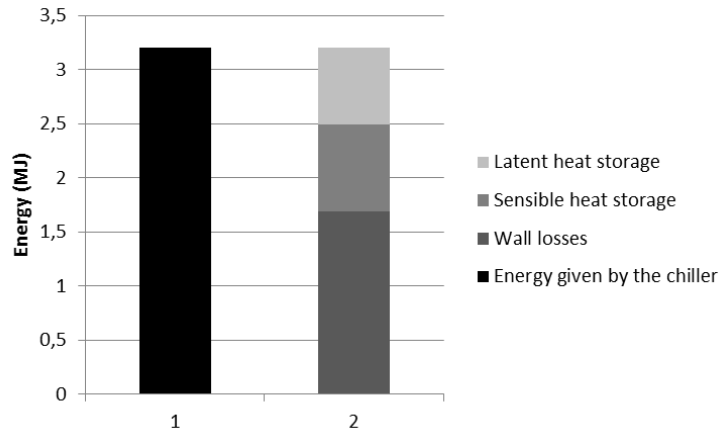


Figure 9: Energy distribution in the system for 11% vol hydrate slurry

The previous Figure 9 shows the comparison between the obtained data with the model concerning the transferred energy to the tank and the sum of the stored energy by latent and sensible heat in the system and the lost energy for slurry with 11% vol. As shown previously this result enables to verify the energy conservation calculated with the model. Furthermore, even with a low solid particles rate, the latent storage is almost equivalent to the sensible heat, which confirms the interest of two-phase fluids in the field of thermal storage. Besides, the losses are more important in Figure 9 (with the loop) than in the previous Figure 8 (without loop). This can be explained by a poor insulation of the loop contrary to the tank. In order to observe more precisely the sources of the different losses on the system, the following Figure 10 shows the distribution of the wall losses on the tank and the loop.

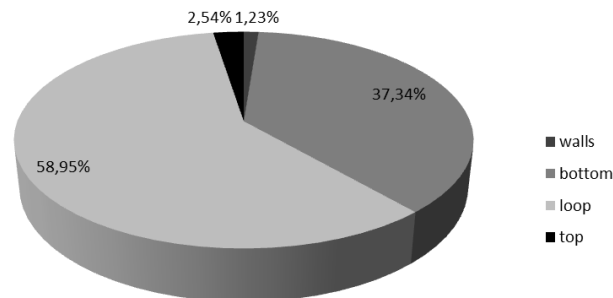


Figure 10: System loss distribution

As shown in Figure 10, the most important loss comes from the loop. The bottom of the tank is also a big source of losses. As previously cited, the losses come from a lack of insulation in the system. Nevertheless it is interesting to observe that insulated walls present very few losses. We can confirm that the insulation of the whole system can have a great impact on the stored energy and specially increase the storage efficiency.

## 5. CONCLUSION

In the present study, a numerical model was developed in order to represent the thermal behaviour of one-phase and two-phase fluids (hydrate slurries) with temperature and pressure variations inside a stirred storage tank. The model takes into account the solid particles rate of CO<sub>2</sub> hydrate slurries evaluated with a CO<sub>2</sub> balance on the system. This model could determine the amount of energies used for hydrate formation but also for thermal storage by latent and sensible heat. Various efficiencies were calculated for various solid particle rates allowing the interest of two-phase fluids in the field of secondary refrigeration to be evaluated. The modelling of hydrates formation was checked by experimental data. In further work, it could be interesting to study hydrate dissociation stage in order to determine the quantity of energy that hydrates are able to release.



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