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## DTA characterization of TBPB and TBPB-CO<sub>2</sub> hydrates in porous media

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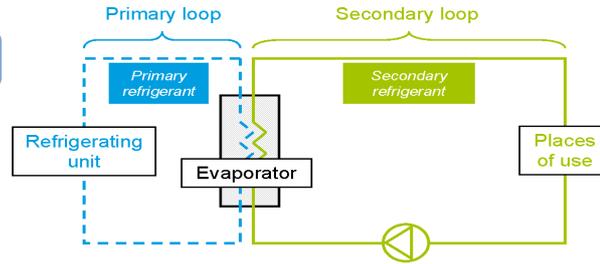
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## Context

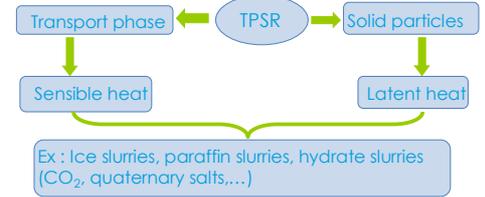
- Reduction of greenhouse-effect primary refrigerants (HFC)

## Secondary refrigeration

- HFC confinement in engine room
- Neutral fluid for distribution



## Two-Phase Secondary Refrigerant



## Objectives of this study

- Coupling between a storage device and a multi temperature cold system  
Modeling/Conception of an unique hydrate storage at various temperature levels

## Interest of hydrate slurry for refrigeration

- Crystals with high melting latent heat: up to ice
- $T_{eq} > 0^{\circ}\text{C}$  suitable for air conditioning and refrigeration
- No mechanical generation

## Previous studies in Irstea

- $\text{CO}_2$ +additives
- Rheology hydrate slurries in flow

## Experimental set-up: 1 DSC and 1 DTA device

- Sensors of T, P
- Thermal studies
- Solid hydrate fraction calculated from a mass balance on  $\text{CO}_2$



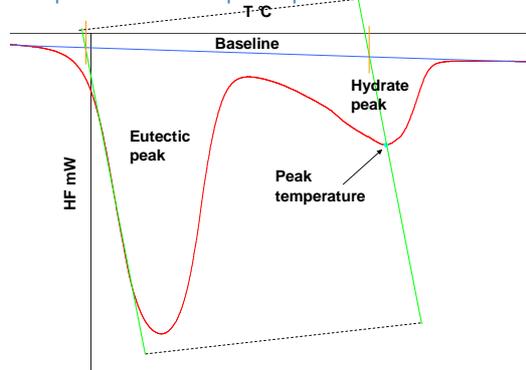
DSC device



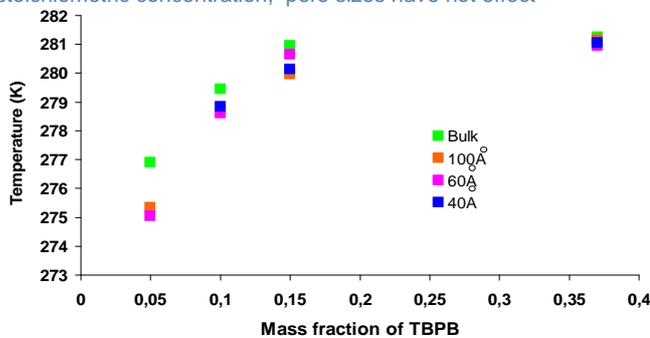
DTA device

## Equilibrium conditions of TBPB hydrate in porous media

The method of extrapolation temperature is used to determine the dissociation temperature at atmospheric pressure on DSC curves



Dissociation temperature in porous media is lower than bulk media. At stoichiometric concentration, pore sizes have not effect

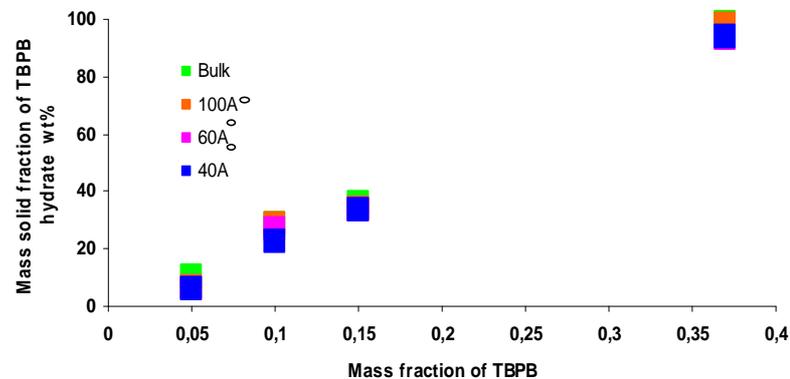


## Determination of solid mass hydrate fraction

Hydrate mass fraction is determined by a calorimetric method, based on the composition of TBPB hydrate.

$$x_h = \frac{\Delta H_{total} - \Delta H_{ice}}{\Delta H_{ice} - \Delta H_{hydrate}}$$

Porous media are a high specific surface. The formation of hydrates in porous media have to improve. The results show that the amount formed in porous media is equivalent to bulk media although the formation is more difficult.



## CONCLUSION

- Porous media is a hydrate inhibitor. Due to the capillary effects it is more difficult to form hydrates in pore.
- Dissociation temperature shift down in porous media. At a given concentration of salt and given pressure, melting temperature is lowest when the pore radius is minimal. That could be an interesting way for the multi temperature storage
- Amount of hydrate formed in porous media is equivalent to bulk phase. For each concentration, maximum hydrate formed is obtained at the largest pore size

## PERSPECTIVES

- Currently, a thermal analysis is in progress to complete the characterization of TBPB in presence of  $\text{CO}_2$  on DTA device

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