# In-situ Study of the Thermal Properties of Hydrate Slurry by High Pressure DSC

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## Abstract

Knowing the enthalpy of hydrate slurry is very essential for energy balance and industrial applications. No direct measurement processes had been developed in this field in the past time. A new experimental method with special device has been developed to carry out on-line measurement of the thermal properties for hydrate slurry under dynamic conditions. With this special device, it is possible to deliver the hydrate slurry to the high pressure DSC (Differential Scanning Calorimetry) directly from the production tank or pipes. Thermal data acquisition will be performed afterwards by DSC. The investigated conditions were at pressure of 30 bar and temperature 0~+7°C. The dissociation enthalpy of $CO_2$ hydrate slurry was about 54 kJ/kg, corresponding 10.8% of solid fraction. The on-line measurement results for $CO_2$ hydrate slurry give a good tendency to apply this phase change slurry to the industrial refrigeration process.

## **Keywords**:

Multi-functional fluid, Phase change slurry, hydrate slurry, on-line measurement, dissociation enthalpy

# 1. Introduction

The impact of synthetic refrigerants on the environment as well as the legal safety obligations drive the refrigeration industry to seek for new ways for completely phasing out greenhouse gases or for decreasing their charge in miscellaneous installations. In order to be free from synthetic refrigerants, industries are continuously searching for environmentally friendly and suitable new technologies that will enable high energy savings, therefore reducing indirect $CO_2$ emissions.

During the last ten years both the load reduction of the refrigerants in the installations and the use of natural, non-flammable, environmentally friendly refrigerants have been the preferred options by many end users such as Nestlé, Unilever, Coca Cola, etc.

An interesting solution could be the use of indirect cooling technology. Secondary coolants ("brines") are aqueous solutions used in various applications. The main advantage with the ice slurry technology is to benefit from high enthalpy due to phase change when slurry melts. Ice slurry is the most used TPSR (two-phase secondary refrigerants) technology. However, ice slurry generation is power limited. The mechanical generators with scraped surface currently on the market have low cooling capacity. (e.g. max module of 80 kW packslurry of HK Refrigeration).

The present work investigates $CO_2$ hydrate slurry, based on $CO_2$, an inoffensive gas (potential of the ozone depletion layer: ODP = 0 and greenhouse effect: GWP (100a) = 1) in order to produce and to use $CO_2$ hydrate slurry continuously. Note that here $CO_2$ is recovered from existing industrial processes (for example fermentation) and is not specially produced for the purpose. The process could contribute to replace polluting fluids that will be prohibited from 2010 in the EU countries on. Consequently, a high potential market is arising.

$CO_2$ hydrate slurry is produced by high pressure $CO_2$ gas injection in a cooled water solution. As a newly developed Temperature Phase Change Secondary Refrigerant (TPSR), $CO_2$ hydrate slurry must contain sufficient solid crystals in suspension to release enough latent heat as a cold source. Besides, the solid fraction will not affect the flowing conditions of hydrate slurry. In the previous studies for $CO_2$ hydrate, the dissociation enthalpy of $CO_2$ hydrate investigated by using Clapeyron equation, DTA and DSC techniques was about 500 kJ/kg which is higher than ice of 333 kJ/kg [1, 2, 3]. The melting point of $CO_2$ hydrate slurry is adjustable according to the production conditions and can be applied to positive temperature range (+5°C or +7°C or even higher) in the field of air-conditioning.

The conventional way to understand the thermal properties of phase change gas hydrate is to complete formation and dissociation of hydrate slurry in the high pressure cell of high pressure DSC (Differential scanning calorimetry) under static conditions. Such methods are widely adopted in the world at present.

Sandrine Marinhas et al [3] used multi-cycle mode of crystallization of $CO_2$ hydrate to accelerate the formation process of $CO_2$ hydrate in the high pressure cell of SETARAM DSC 111. They used a fixed amount of distilled water, applied static gas pressure and without any agitation. Their measurement about the dissociation enthalpy of $CO_2$ hydrate has good agreement with previous studies. However, solid fraction and available latent heat of $CO_2$ hydrate slurry were estimated only by equations. Under their experimental conditions, the hydrate volume fraction was estimated at 2.8%, the possible calculated enthalpy of $CO_2$ hydrate slurry is of $1.15\times104$ kJ/$m^3$.

Obviously, this method can't be applied to dynamic conditions when hydrate slurry is undergoing of transportation since hydrate slurry is a complex compound with free water, hydrate solid and micro bubbles under high pressure.

Under dynamic production conditions, hydrate slurry is a complex compound with free water, hydrate solid and micro bubbles under appropriate pressure and temperature. The knowledge of the solid fraction as well as the available latent heat of this multiphase fluid is essential for cooling industry. However, direct measurement processes are little developed in this field.

In this paper, to carry out on-line measurement of the thermal properties of $CO_2$ hydrate slurry by using the special sample device of µDSCVII SETARAM is proposed.

# 2. Materials and methods

## 2.1. Description of the DSC device

The MicroDSC technology is based on symmetrical heat-flux design, according to the Calvet principle. The transducers made of semiconductors are located inside a thermostated bulky calorimetric block, fully surrounding the experimental vessels (See Fig1). This design ensures a high sensitivity and an excellent level of precision to MicroDSC.

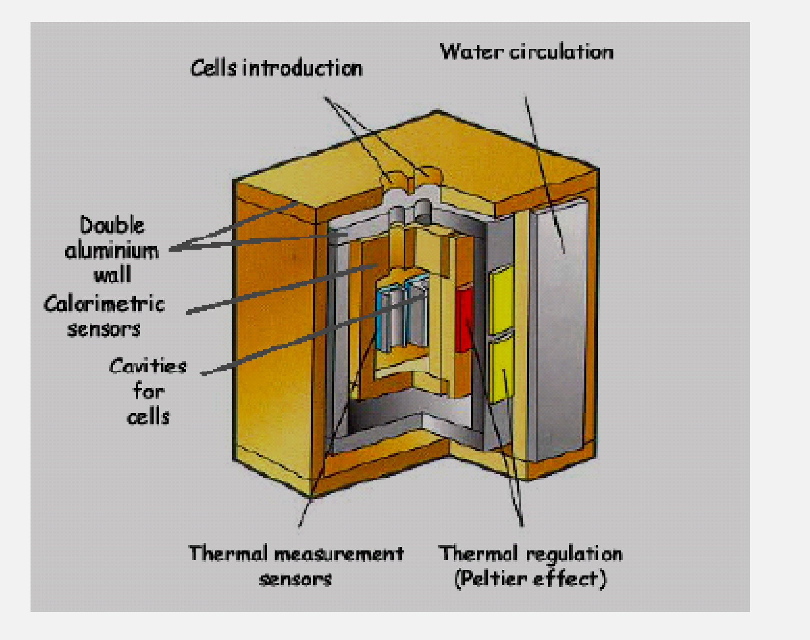

*Fig1. Schematic of MicroDSC Calorimeter Block*

The working principle of MicroDSC is based on: In the heat flux DSC (a Tian-Calvet type microcalorimeter), thermal effects are measured by two fluxmeters (one on the measurement side and one on the reference side), each of which measures the thermal power exchanged at each moment between the vessel and the calorimetric unit. The Tian-Calvet fluxmetric transducer envelopes the sample, making it possible to measure almost all the exchanges between the vessel and the unit. The differential power required to heat the sample compared to the reference at the same scan rate is thus recorded. This capability gives this device a clear metrological advantage in terms of both the quantity of measurements and their sensitivity (see Fig2).

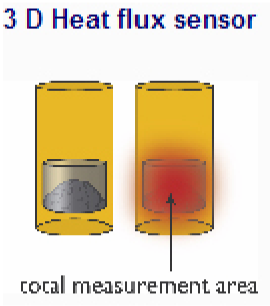

*Fig2. Schematic of DSC working principle*

High pressure DSC experimental set-up is based on a µDSCVII differential micro-calorimeter from Setaram (see Fig3). Gas high-pressure panel including a one-stage compressor provides gas feeding with constant regulated pressure. Cooling of the DSC furnace is performed by Peltier modules, with a circulation of refrigerated water as a cold source. The temperature range of operation is 228 to 393 K. Heat flow measurement is based on the Calvet principle. The fluxmeters used to ensure a high sensitivity and an excellent level of precision to the DSC calorimeter.

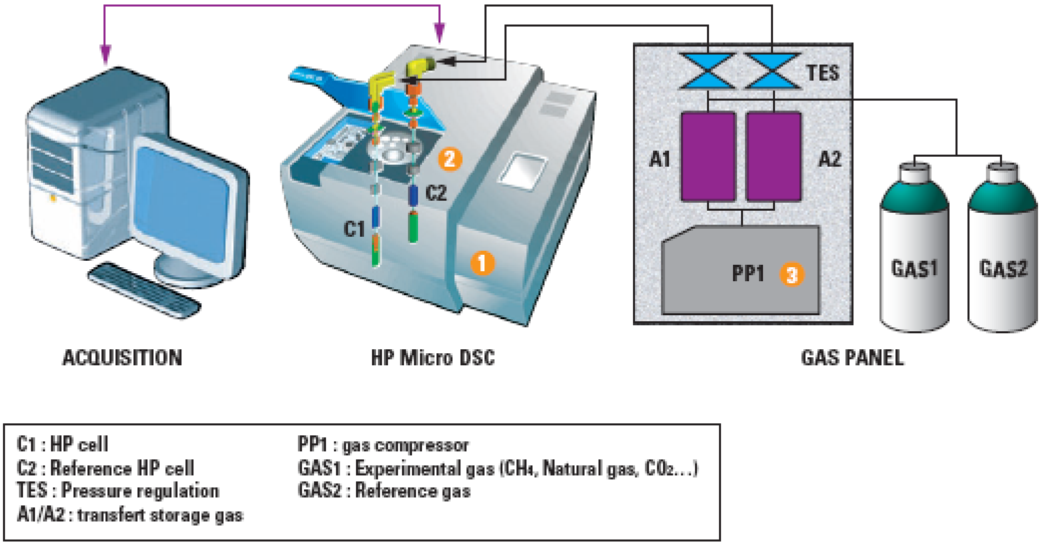

*Fig3. Schematic of high pressure DSC experimental set-up*

The specially designed hydrate slurry sampling device consists of a gas-tight high pressure cell made of Hastelloy C276, which allows the analysis of corrosive fluids. It has an internal volume of about 0.5 cm$^3$ and a maximum operating pressure of 40 MPa. The screwed top is equipped with a doughnut ring coupled to an antiextrusion ring. It is welded to a thermal line; hydrate slurry flows into high pressure cell through hydrate slurry sampling tube which has 2mm diameter. After filling the high pressure cell, the overflowing hydrate slurry exits through the hydrate slurry overflowing exit. Such device connects with hydrate slurry production unit through specific high pressure connection (see Fig4).

Classically, high pressure cells are filled by means of a spatula in the case of solids or a pipette in the case of liquids. The vessel has to be weighted before and after filling, in order to precisely determine the mass of sample to be analyzed. The reference vessel can be empty or filled with an inert material in order to compensate for the differences in heat capacity between the two vessels. The inert material can be alumina (for powders) or silicone oil (for liquids) or model data for simple solutions.

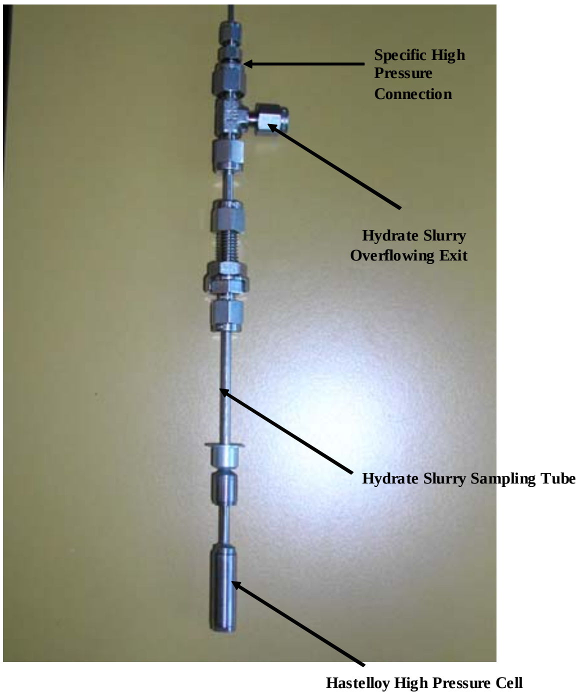

*Fig4. Special $CO_2$ hydrate slurry sampling device*

## 2.2. Description of the $CO_2$ hydrate slurry sampling

A new test bench has been designed and built. The experimental loop mainly consists of a hydrate generator of a closed loop circuit of hydrate slurry which was directly transported to µDSCVII high pressure cell through pipes and specific high pressure connection (see Fig 5).

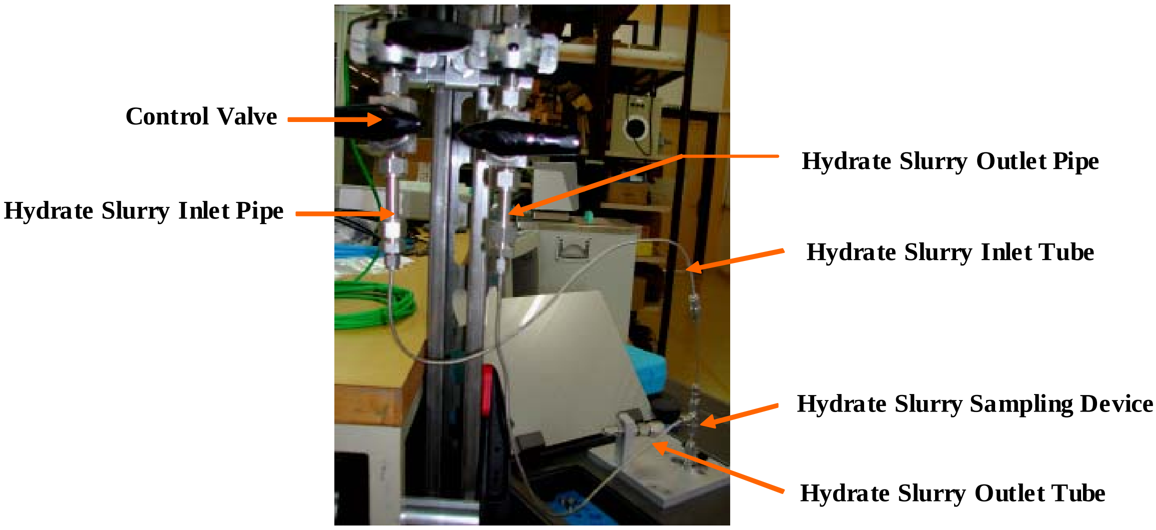

*Fig5. Connections between DSC and $CO_2$ hydrate slurry production loop*

## 2.3. Sample acquisition

$CO_2$ hydrate slurry was created in the tank under conditions of 30 bar, 1~2°C. Fig6 shows the appearance of $CO_2$ hydrate slurry. Since the formation of gas hydrate is an exothermic equilibrium process, which will increase temperature of $CO_2$ hydrate slurry very much in very short time. The temperature of $CO_2$ hydrate slurry will be 4~6°C when it reaches the high pressure cell of µDSCVII. The volume of the high pressure cell is about 0.508ml. The density of hydrate slurry was obtained from Mass Flow meter. Such information will be used to determine the mass of $CO_2$ hydrate slurry in the high pressure cell when the high pressure cell is full of $CO_2$ hydrate slurry. Our previous experiments show that the $CO_2$ hydrate slurry will dissociate at 8~10°C. Therefore, the temperature of DSC furnace was set at 4°C or lower which will preserve $CO_2$ hydrate slurry from dissociation.

*Fig6. Appearance of $CO_2$ hydrate slurry*

The high sensitivity of the microDSCVII calorimeter requires a meticulous cleaning of cells between each analysis. Humidity or finger traces on the walls or in the sealing system can lead to thermal signals of interference during the analysis. High pressure cell as well as reference were be cleaned several times by acetone before and after the filling with the sample. The reference cell was filled up with distilled water. The high pressure cell was empty before the injection of hydrate slurry.

The scan mode RAMP was adopted. Each scan consisted of a cooling at the faster rate 1.2 K/min to 4 ºC followed by duration of isotherm stabilization of twenty minutes. Finally, the sample was heated up at 0.1K/min till 25 ºC until complete dissociation of hydrate in the high pressure cell. The dissociation peak of $CO_2$ hydrate was integrated and calculated by software SETSOFT2000. In the final, the dissociation enthalpy of $CO_2$ hydrate slurry was obtained. The solid fraction of $CO_2$ hydrate slurry was estimated.

# 3. Experimental Results

Fig7 shows the heat flow of the dissociation process of $CO_2$ hydrate slurry. After twenty minutes stabilization, the sample was heated up to 25 ºC in order to detect the dissociation of gas hydrate. The peak area of the recorded signal (generally called a “thermogram”) is related to the heat flow generated or absorbed by the sample. From the curve, one dissociation peak of exothermic equilibrium process was observed.

By integrating the area of the dissociation peak with SETSOFT2000, 54 kJ/kg of enthalpy was obtained. As the result of dissociation enthalpy of $CO_2$ hydrate mentioned by Laurence Fournaison *et al* [3] was 500 kJ/kg. Thus, the solid fraction of $CO_2$ hydrate in the hydrate slurry is about 10.8%. At this temperature range, the enthalpy density for the pure water at that temperature is around 8 kJ/kg.

Fig7 also shows that the dissociation of $CO_2$ hydrate slurry began around 10°C and finished around 11°C. The observation of dissociation temperature $CO_2$ hydrate slurry in the experimental loop was between 8°C~10°C.

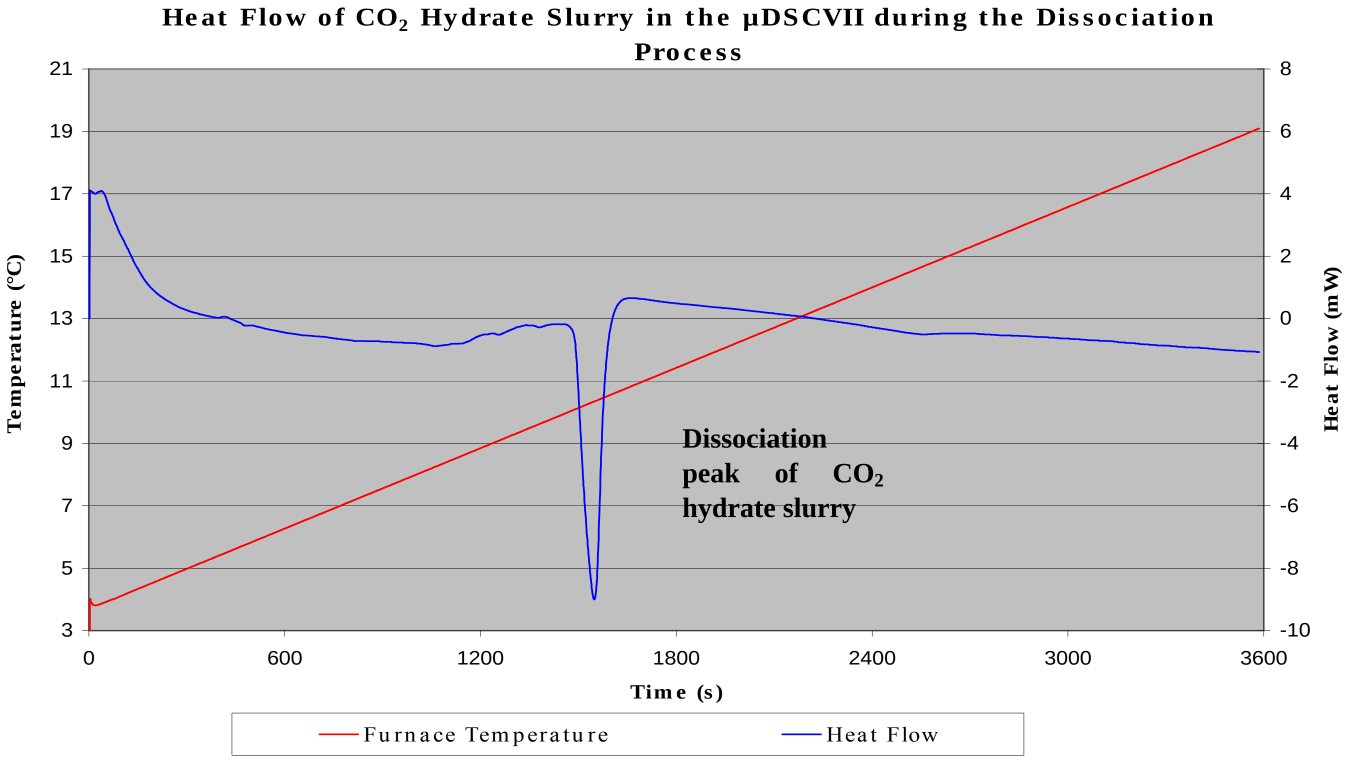

*Fig7. Heat Flow of $CO_2$ hydrate slurry in the* µDSCVII *during the Dissociation Process*

# 4. Discussion

As µDSCVII is a very sensitive machine. Heating speed has large influence on the dissociation peaks of hydrate slurry. According to the experimental results of PCM with DSC, heating at rather low speed will have much better appearance of dissociation peaks. This may also be applicable to hydrate slurry.

µDSCVII provides more accurate result about dissociation temperature since µDSCVII excludes any ambient influence on dissociation process and µDSCVII controls temperature of furnace very precisely while in the experimental loop, so many factors will disturb the observation of dissociation temperature like pressure drop, insulation, transportation, high pressure pump, mechanical force…etc.

It is rather difficult to know exactly how the high pressure cell is filled during on-line process. So it will be very hard to determine the CO2 hydrate slurry mass accurately in the high pressure cell to have very accurate results regarding the CO2 hydrate slurry dissociation enthalpy. Nevertheless, the estimated value of the dissociation enthalpy of CO2 hydrate slurry approaches the real value.

To have accurate results, the best would be to use a greater amount of CO2 hydrate slurry mass. However, this is not applicable to high pressure DSC for the time being which works only with minor amount.

## 5. Conclusions and Outlook

On-line measurement of enthalpy of $CO_2$ hydrate slurry is feasible. This technique can be applicable to other kinds of gas hydrate slurry in determination of enthalpy as well as specific heat capacity. The enthalpy of $CO_2$ hydrate slurry is estimated about 54 kJ/kg which corresponds to 10.8% of solid fraction. The dissociation temperature of $CO_2$ hydrate slurry observed by µDSCVII has good agreement with results obtained from experimental loop.

In this paper, the first experimental enthalpy density measurement was shown. But a basic understanding of the procedure is necessary to improve the results. This will lead to the highest possible quality of results obtainable with this measuring technique. The evaluation of the dissociation curves at different heating rate and different solid fraction under different operation conditions are on going.

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## References

1. Graydon K. Anderson, “Enthalpy of dissociation and hydration number of carbon dioxide hydrate from the Clapeyron equation” J. Chem. Thermodynamics, 35 (2003) 1171–1183

2. Laurence Fournaison, Anthony Delahaye and Imen Chatti, Jean-Pierre Petitet, $CO_2$ hydrates in Refrigeration Processes, Ind.Eng.Chem.Res.2004, 43, 6521-6526

3. Sandrine Marinhas, Anthony Delahaye, Laurence Fournaison, Didier Dalmazzone, Walter Fürst, Jean-Pierre Petitet, Modelling of the available latent heat of a CO2 hydrate slurry in an experimental loop applied to secondary refrigeration, Chemical Engineering and Processing 45 (2006) 184–192