




Open Archive Toulouse Archive Ouverte

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/21870>

To cite this version:

Torré, Jean-Philippe  and Hailot, Didier and Marlin, Laurent and Plantier, Frédéric and Dicharry, Christophe and Delroisse, Henry and André, Rémi and Lilova, K. *Mechanically agitated calorimetric cells working under pressure at macro and micro scale: application to gas hydrates*. (2017) In: 9th International Conference on Gas Hydrates (ICGH9), 27 June 2017 - 30 June 2017 (Denver, United States).

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Mechanically agitated calorimetric cells working under pressure at macro and micro scale: application to gas hydrates

J.-P. Torr ^{1*}, D. Haillot², L. Marlin³, F. Plantier¹, C. Dicharry¹, H. Delroisse¹, R. Andr ⁴, K. Lilova⁵

¹ CNRS/Total/Univ Pau & Pays Adour, Laboratoire des Fluides Complexes et leurs R servoirs-IPRA, UMR5150, 64000, PAU, France.

² Univ. Pau & Pays Adour   EA1932   LaTEP   Laboratoire de Thermique Energ tique et Proc d s, Rue Jules Ferry, BP7511   PAU, F-64075, France

³ Institut Pluridisciplinaire de Recherche Appliqu e dans le domaine du g nie p trolier (IPRA). Atelier de physique. Avenue de l'Universit , BP 1155   PAU, F-64013, France.

⁴ SETARAM Instrumentation, 7 Rue de l'Oratoire, CALUIRE, F-69300, France

⁵ SETARAM Inc., Valley Business Park, Suite 22, 216 US Highway 206, Hillsborough - NJ 08844-4384, USA

* Corresponding author: jean-philippe.torre@univ-pau.fr

Abstract

Originally applied to fields related to oil and gas production and flow assurance, high pressure differential scanning calorimetry (HP-DSC) has now been involved in several new studies such as carbon dioxide sequestration by CO₂/CH₄ exchange in naturally occurring gas hydrates or CO₂ hydrate reversible formation/dissociation for refrigeration loops. However, the technique still has some limitations, which are linked to the fact that the gas hydrate formation occurs at the gas/liquid interface, and because the hydrate nucleation can be rather difficult in small volumes especially in quiescent conditions. It leads to several problems such as inefficient gas dissolution, long induction times, formation of a hydrate crust covering the gas/liquid interface, low hydrate to water conversion, etc. As a result, it is very difficult to determine accurately the heat capacities and the kinetics of formation/dissociation of several systems involving gas hydrates.

This study presents two prototypes of calorimetric cells equipped with an in-situ mechanical agitation system, which allow performing experiments under pressure (150 bar maximum for the cells used in this work). The first system presented, called MIXCEL[ ], was developed for macro-calorimetry analysis (experiments carried out with a BT 2.15 Calvet Calorimeter from SETARAM Instrumentation). Very recently, we have developed a novel prototype of micro-calorimetric agitated cell (called MICROMIXCEL[ ]) for microDSC analyses (experiments carried out using a microDSC7 evo from SETARAM Instrumentation). Both technical aspects, and results obtained at macro and micro scales with gas hydrate systems are presented and discussed.

For MIXCEL[ ], the cell body, in which the sample can be inserted, is a 17mm outer diameter stainless steel cylinder with an internal volume of approximately 7 cm³. Mechanical stirring in the measuring cell is provided by a screwable stirrer. It is interchangeable and several stirrer designs can be used. For this study, a three-staged impeller composed by three 2-blades curved turbines was used, which can rotate up to 500 RPM. The link between the wellhead and the measuring cell is provided by two concentric tubes allowing the stirring rod to rotate freely in the tubes. On the upper part of the system, a magnetic coupling allows linking a DC motor (ATEX standards) to the shaft. The fluids (i.e. gases) are injected in or out of the cell by means of two nozzles located on the sides of the upper part.

For MICROMIXCEL[ ], the measuring cell is a HP cell made of stainless steel with a 0,33 cm³ internal volume. A mechanical stirrer, which is a custom type anchor, is screwed to the shaft and can rotate inside the cell at several hundreds of RPM. The measuring cell is connected to the upper part of the system by HP tubing. The agitator shaft is located in this tubing. Two nozzles are inserted on the upper part to allow for gases inlet and outlet. Note that, in

contrast with the MIXCEL®, only one HP tube is present around the shaft (no concentric tubes) for the inlet and outlet gas circulation. A small DC motor equipped with a hand-made magnetic coupling allows the rotation of the agitator.

For the two agitated cells, and for several complex systems such as ice slurries or clathrate compounds (i.e. CO₂ hydrates, mixed THF-CO₂ hydrates), we have demonstrated by performing experiments in comparison with the same cells without agitation, that the effect of the in-situ agitator reduces the crystallization metastability, increases the water to hydrate conversion and lowers efficiently the time for analysis. We have showed the potential of such technologies for thermodynamic studies by obtaining very easily hydrate phase equilibrium data under pressure. We have also performed a detailed study of the cyclopentane (CP) hydrate, as this system is very hard to analyze with non-agitated calorimetry techniques due to very low water to hydrate conversion. Interestingly, we have obtained, both at macro and micro scales, a very robust value of the phase change enthalpy of this hydrate.

The use of such novel calorimetric cells thus opens a wide range of possibilities for complex systems, such as gas hydrates, which must be analyzed under both pressurized and agitated conditions.