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THERMOPHYSICAL PROPERTIES OF GAS HYDRATES WITH STIRRED, HIGH PRESSURE CALORIMETRIC CELLS

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High pressure differential scanning calorimetry (HP-DSC) is of importance in several fields involving gas hydrates, such as oil and gas production, flow assurance, carbon dioxide capture and storage, CO_2 hydrates reversible formation/dissociation for refrigeration loops.

However, the technique suffered for some limitations linked to the fact that the gas hydrate formation in the calorimetric cell occurs at the gas-liquids interface, leading to problems such as inefficient gas dissolution, formation of a hydrate crust covering the gas/liquid interface, low hydrate to water conversion, and difficulties to crystallize these compounds even at low temperature. It is for example rather difficult to determine accurately the heat capacities and the enthalpies of formation/dissociation of several systems involving gas hydrates.

To overcome such limitations, we present two prototypes of calorimetric cells equipped with an in-situ mechanical agitation system, which allow performing experiments under pressure (150 bar max). The first one is called MIXCEL®, and was developed for macro-calorimetry analysis (experiments carried out with a BT 2.15 Calvet Calorimeter from SETARAM Instrumentation). The second one, called MICROMIXCEL®, was developed for micro-calorimetry analysis (experiments carried out using a microDSC7 evo from Setaram Instrumentation). In this study, technical details of the two cells and results obtained both at macro and micro scales will be presented, and compared to the case with no agitation. Thermophysical properties of the cyclopentane hydrate (phase change enthalpy, and specific heat) will be given and commented. The use of such novel calorimetric cells opens a wide range of possibilities for complex systems, such as gas hydrates, which must be analysed in both pressurized and agitated conditions.