Characterization of gas hydrates formation dissociation using high pressure DSC

INTRODUCTION

The usual way to determine the thermodynamic conditions of the formation of hydrates in drilling mud formulations is to use a PVT cell with visual observation and simultaneous temperature and pressure measurements. This technique requires heavy instrumentation and often cannot be used if solid particles are present in the formulation.
Calorimetry is another way to determine compositions, dissociation enthalpies and heat capacities of hydrates. In order to work under high pressure, an innovative methodology (patent of the French Institute of Petroleum) has been developed using MICROCALVET up to high pressure to determine the thermodynamic properties and kinetics of gas hydrate formation. This technique allows the detection of phase transitions versus time, temperature and pressure.

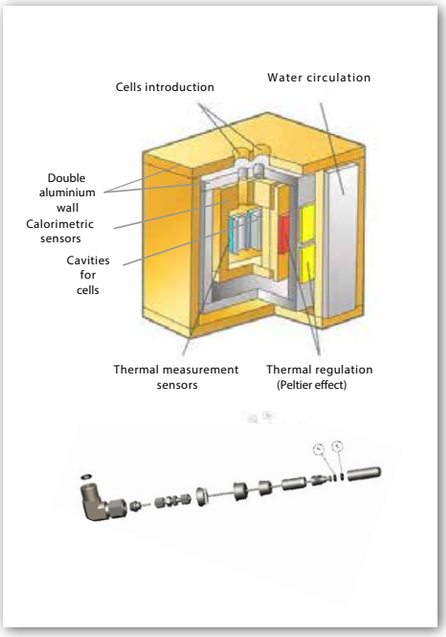

Figure 1: High Pressure MICROCALVET with the high pressure cell and panel

EXPERIMENT

MICROCALVET has a vessel operating with a dedicated high pressure panel (FLEXI HP 1000) up to 1000 bar (14500 psi) and up to 120° C (Figure 1).

The high pressure microcalorimetry technique can be used to investigate gas hydrates in different situations :
- formation of gas hydrates (especially methane)
- investigation of gas hydrates trapped in marine sediments
- plugging of annulars (offshore extraction) by hydrate formation in drilling muds
- storage and transportation of natural gas using gas hydrate
-gas hydrate formation and dissociation for cold storage

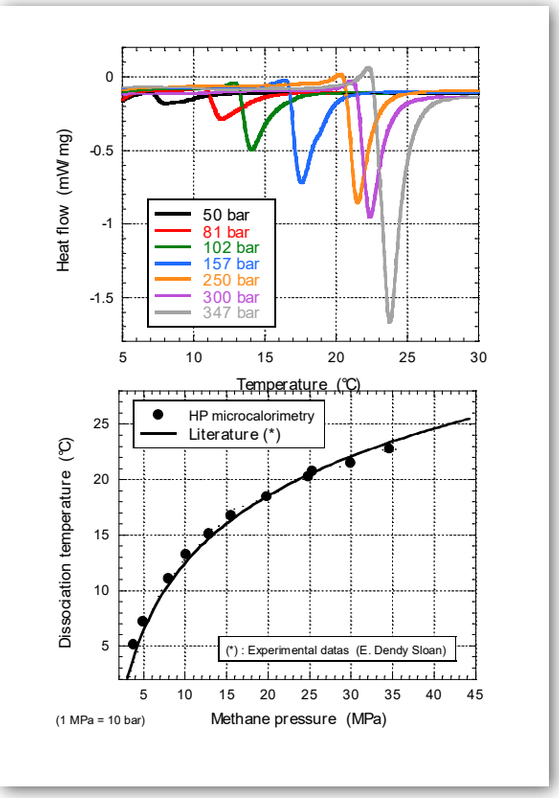

Figure 2: Methane hydrate dissociation in deionised water and stability curve up to 400 bar
Reference : C. Dalmazzone et al., Journal of Thermal Analysis and Calorimetry, Vol. 78 (2004) 165–172

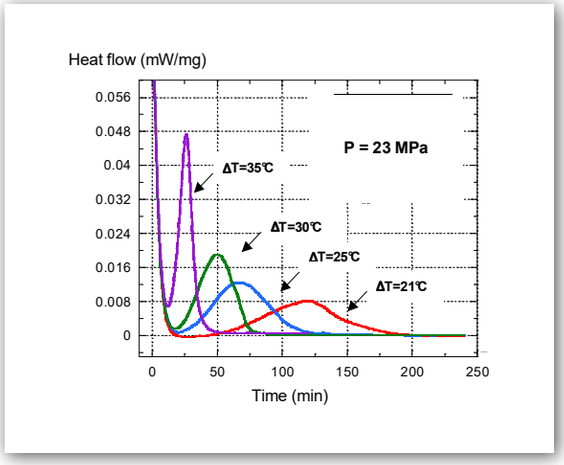

Figure 3: Isothermal formation of methane hydrates at 230 bar
Reference : D. Dalmazzone, N. Hamed, C. Dalmazzone and L. Rousseau, Journal of Thermal Analysis and Calorimetry 85 (2006) 361-368

RESULTS AND CONCLUSION

Figure 2 shows the methane hydrate dissociation (after formation in deionised water at different pressures of methane). The stability curve shows the very good accordance with the litterature data..
On Figure 3 is presented how the MICROCALVET is used to measure the formation of methane hydrate at constant temperature with variable pressure.on the tested pressure range with a R^2 value of 1.
Figure 4 presents the methane hydrate dissociation (after formation a oil based muds at different methane pressure . Such investigations allow to predict the stability curve of methane hydrates according to the drilling muds used during the operation .

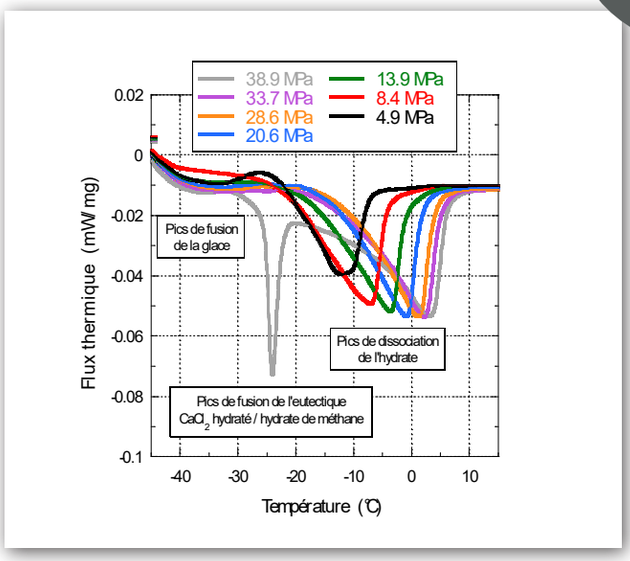

Figure 4: Methane hydrate dissociation in oil based muds

INSTRUMENT

MICROCALVET

-45°C to 120°C

HIGHEST HEAT MEASUREMENT ACCURACY
3D sensor based on thermocouples with Joule effect calibration.

MODIFIABLE TEMPERATURE CONDITIONS
for increased flexibility and replication of real life conditions.

CONVENIENT INTERCHANGEABLE CRUCIBLES AND CELLS
to perform even the most demanding experiments using one instrument :
- high pressure (1000bar) and high vacuum
- pressure measurement and control
- mixing experiment

EXTERNAL COUPLING CAPABILITY
designed to increase your research options including manometry, BET instrumentation, gas analyzers, humidity controllers and gas panels