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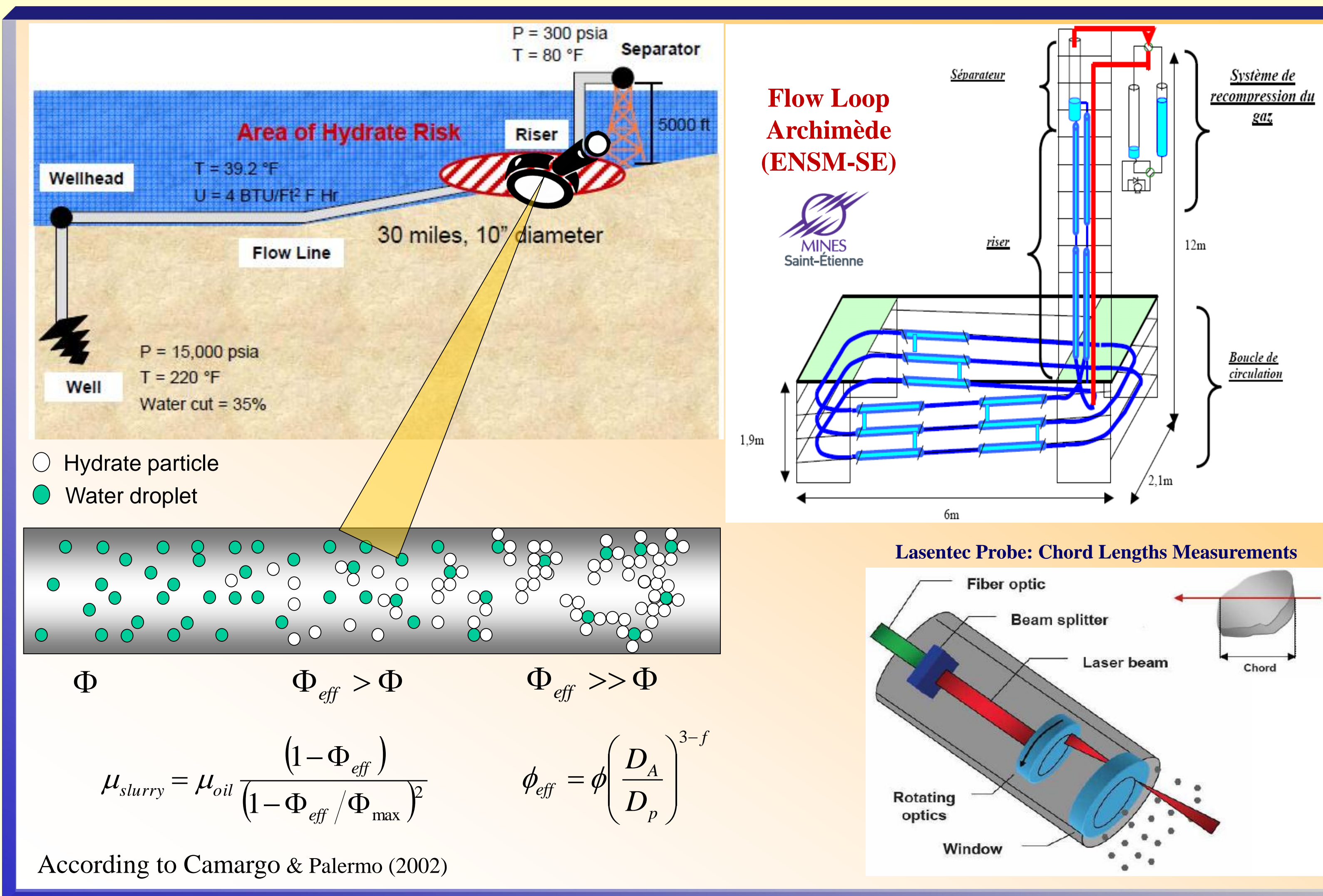
INFLUENCE OF THE CRYSTALLIZATION RATE ON THE FORMATION OF GAS HYDRATES FROM CH₄-C₃H₈ GAS MIXTURES AND EXTENSION TO OTHER MIXTURES

Du LE-QUANG, Baptiste BOUILLOT, Jean-Michel HERRI*

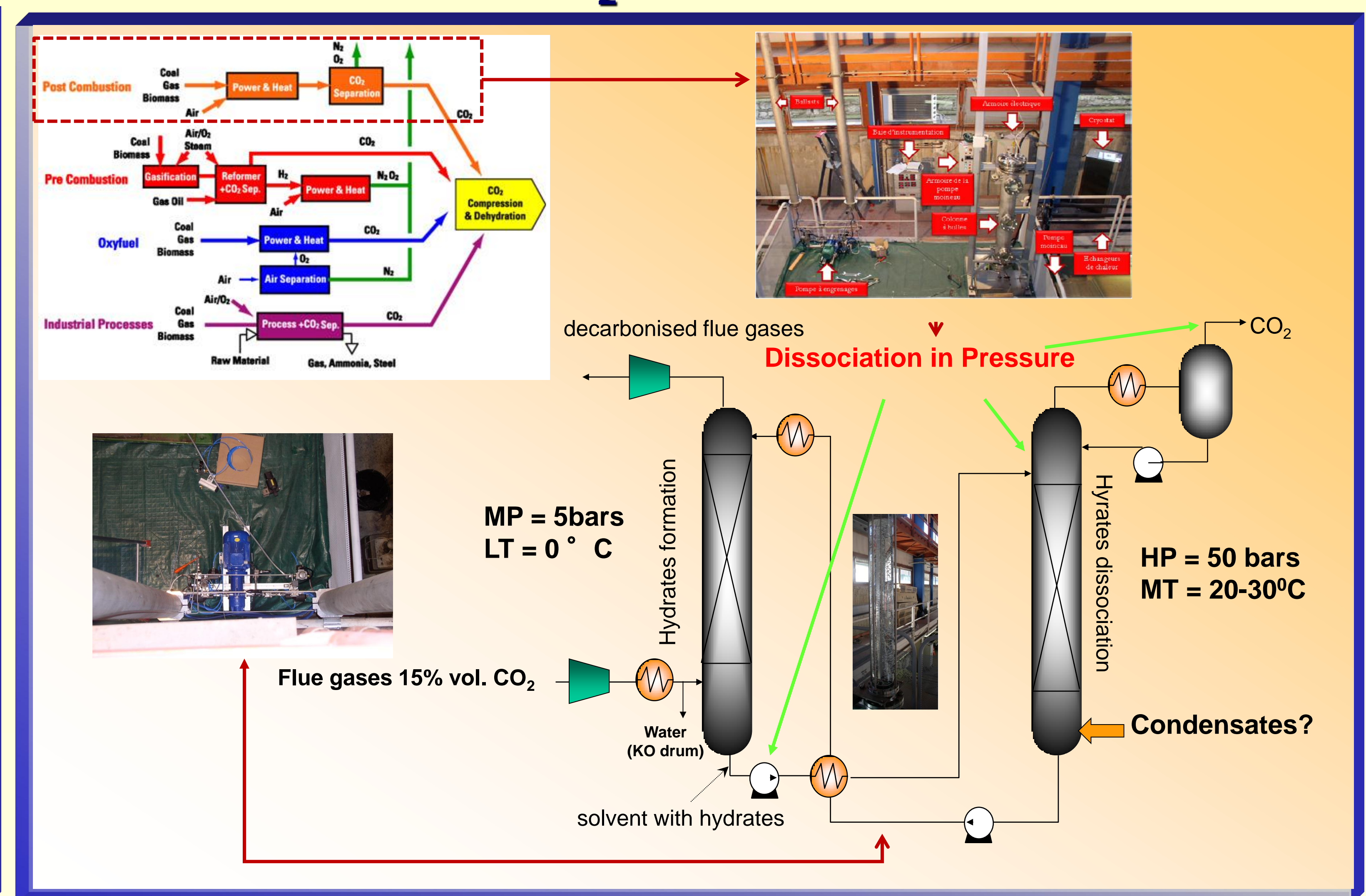
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In this study, we present details on two different experimental procedures to form mixed hydrates. They are applied to measure the volume and composition of the crystallized hydrate from CH₄-C₃H₈ gas mixtures at high and low crystallization rate, respectively. The results obtained from both methods reveal a difference in composition, final pressure and volume between the two procedures (quick and slow crystallization). Furthermore, this work aims at contributing to the global understanding of the coupling between kinetics and thermodynamics to provide some insight in the composition of the gas hydrate phase during its crystallization from an aqueous liquid and a mixed gas phase. In addition, we face new experimental facts that open questioning after comparing the modelling of clathrate hydrates following the classical approach (van der Waals and Platteeuw, 1959).

FLOW ASSURANCE

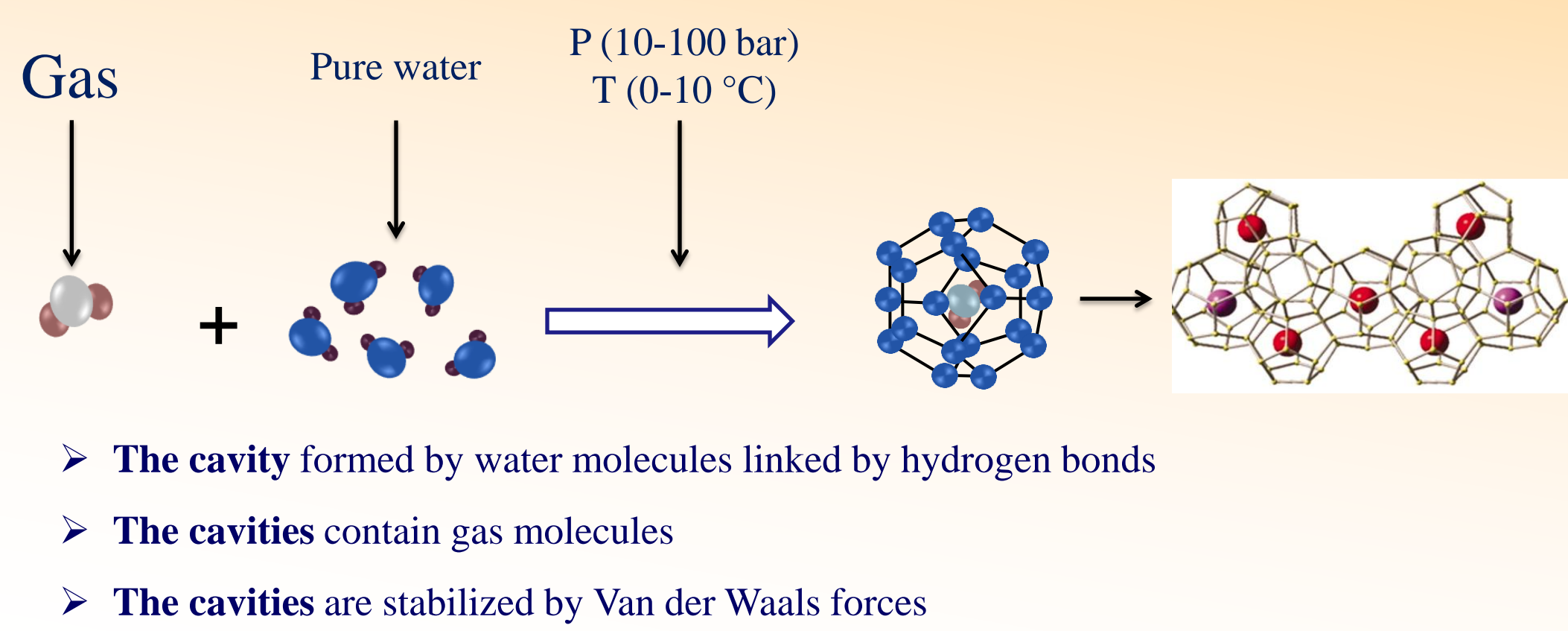


CO₂ CAPTURE

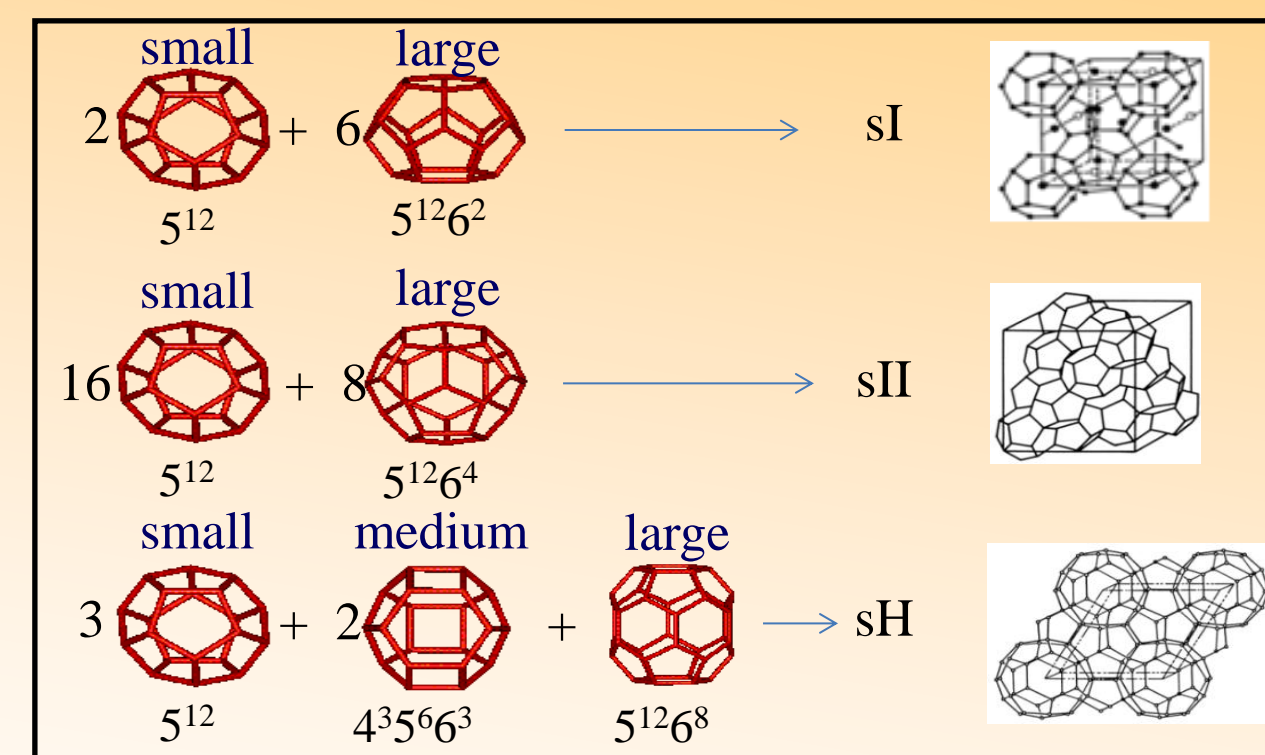


GAS HYDRATES FORMATION

1 - Conditions needed for the gas hydrate to form



2 - Hydrate structure



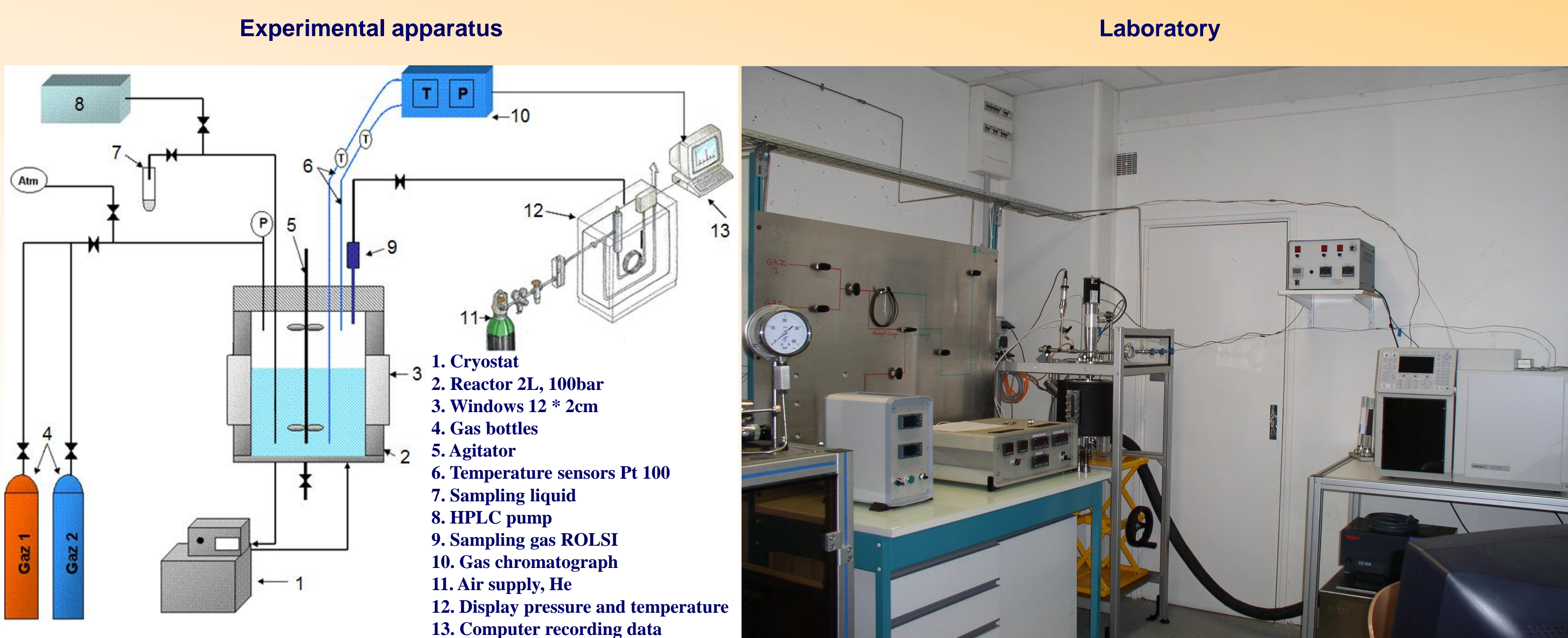
3 - Clathrate hydrate

| Clathrate hydrate structures | S _I | | S _{II} | | S _H | | |
|--|-----------------|--------------------------------|-----------------|--------------------------------|-------------------|--|--------------------------------|
| | Small | Large | Small | Large | Small | Medium | Large |
| Cavity | Small | Large | Small | Large | Small | Medium | Large |
| Description | 5 ¹² | 5 ¹² 6 ² | 5 ¹² | 5 ¹² 6 ⁴ | 5 ¹² | 4 ³ 5 ⁶ 6 ³ | 5 ¹² 6 ⁸ |
| Number per unit cell (m _c) | 2 | 6 | 16 | 8 | 3 | 2 | 1 |
| Average cavity radius (Å) | 3,95 | 4,33 | 3,91 | 4,73 | 3,91 ^c | 4,06 ^c | 5,71 ^c |
| Coordination number ^a | 20 | 24 | 20 | 28 | 20 | 20 | 36 |

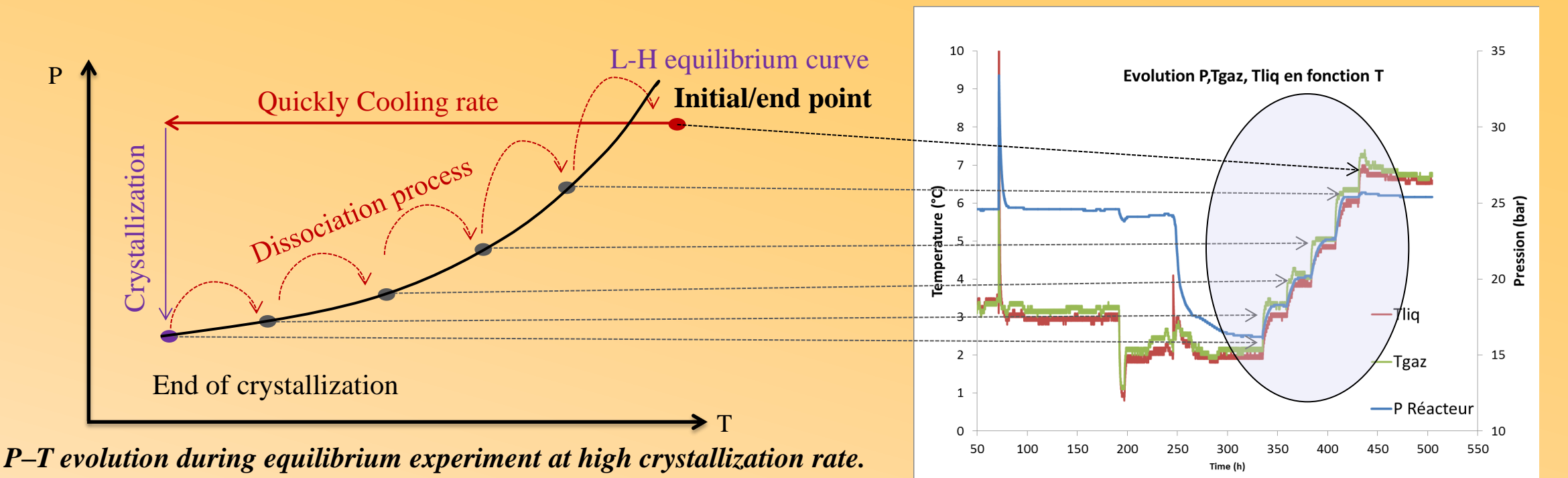
(a) The number of oxygen atom per cavity

Experimental procedure and set-up

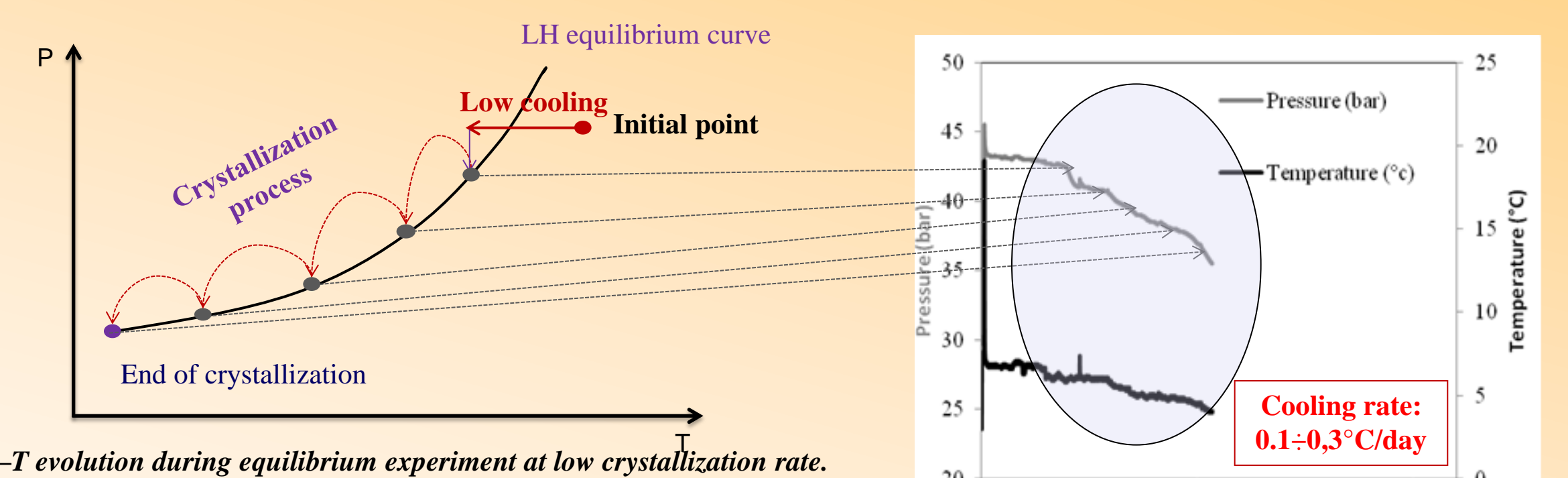
✓ Experimental apparatus and laboratory



✓ Experimental procedure at high driving force



✓ Experimental procedure at low driving force



COMPARING: Results from procedure at high driving force AND procedure at low driving force

Molar composition of the studied gas mixtures (standard deviation about 3%)

| Gas mixtures | Methods | CH ₄ | C ₃ H ₈ | Pint | Tint | Reactor volume | Mass water injected |
|--------------|---------|-----------------|-------------------------------|------|--------|----------------|---------------------|
| | | % | % | MPa | oK | | |
| Gas 1 | Slow | 84.61 | 15.39 | 1.73 | 279.95 | 2.36 | 801.10 |
| Gas 2 | Slow | 84.61 | 15.39 | 1.73 | 279.95 | 2.36 | 801.10 |
| Gas 3 | Slow | 86.86 | 13.14 | 1.83 | 284.95 | 2.36 | 800.94 |
| Gas 4 | Quick | 85.77 | 14.23 | 1.81 | 281.00 | 2.36 | 801.15 |
| Gas 5 | Quick | 85.81 | 14.19 | 1.71 | 280.45 | 2.36 | 801.05 |
| Gas 6 | Quick | 86.89 | 13.11 | 1.77 | 285.05 | 2.44 | 800.94 |
| Gas 7 | Quick | 86.89 | 13.11 | 1.77 | 285.05 | 2.44 | 800.94 |

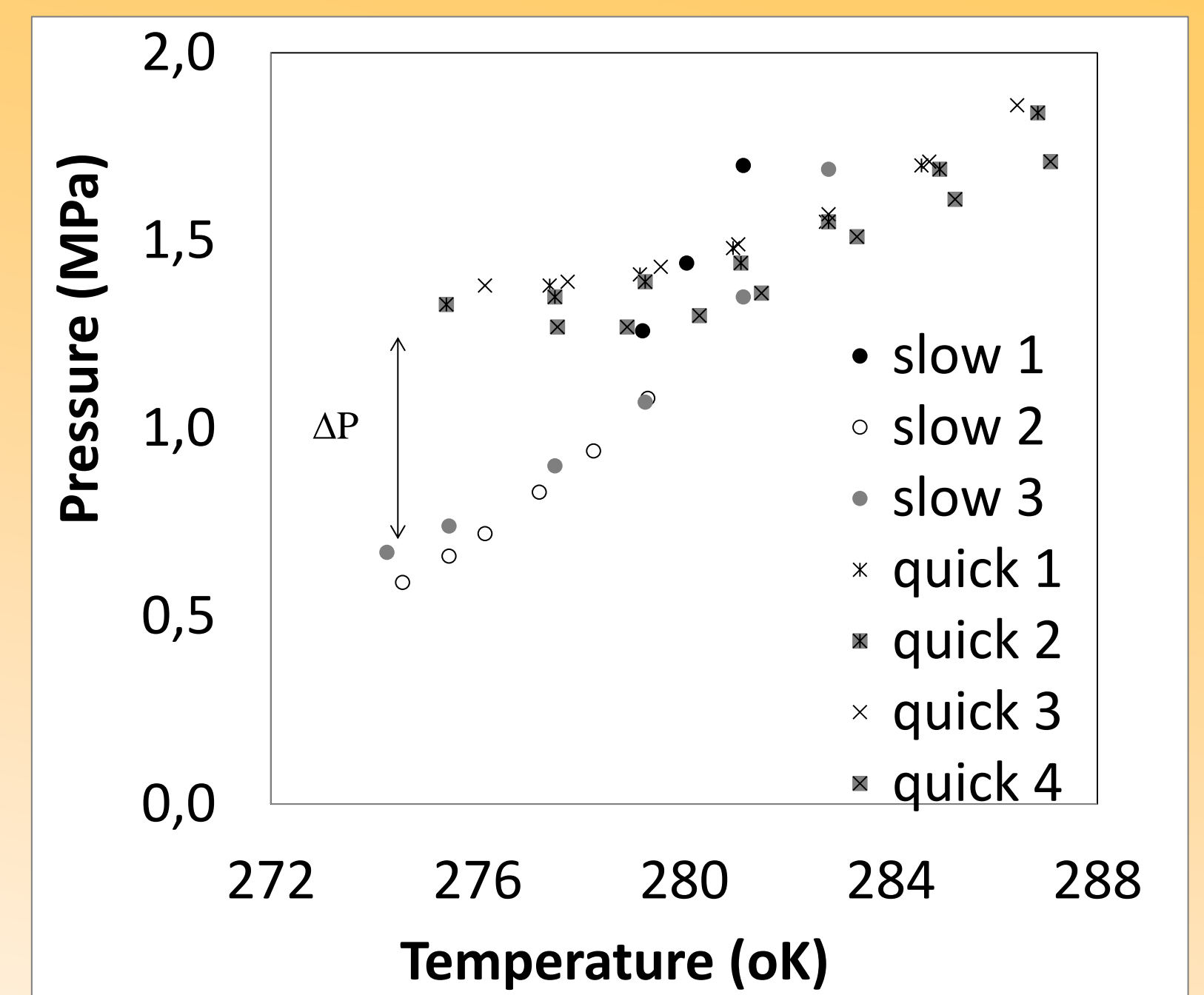
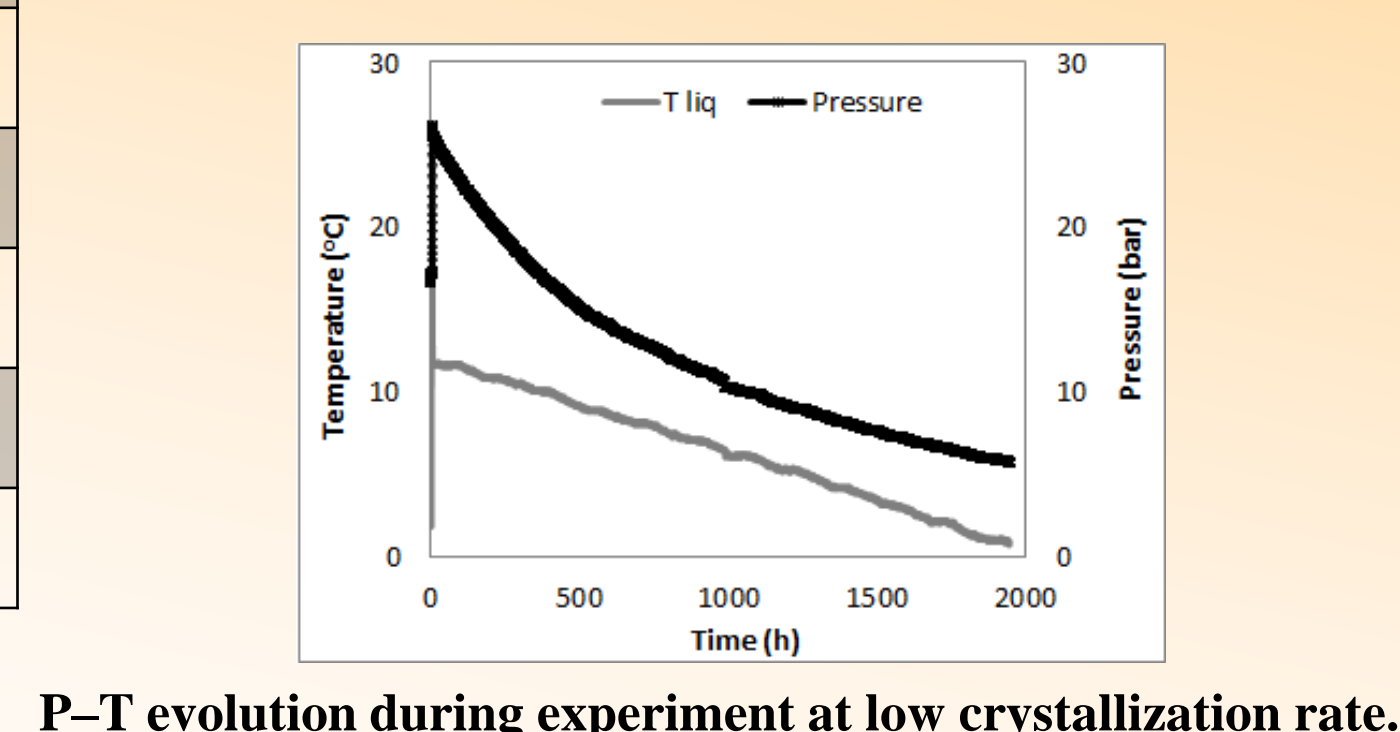
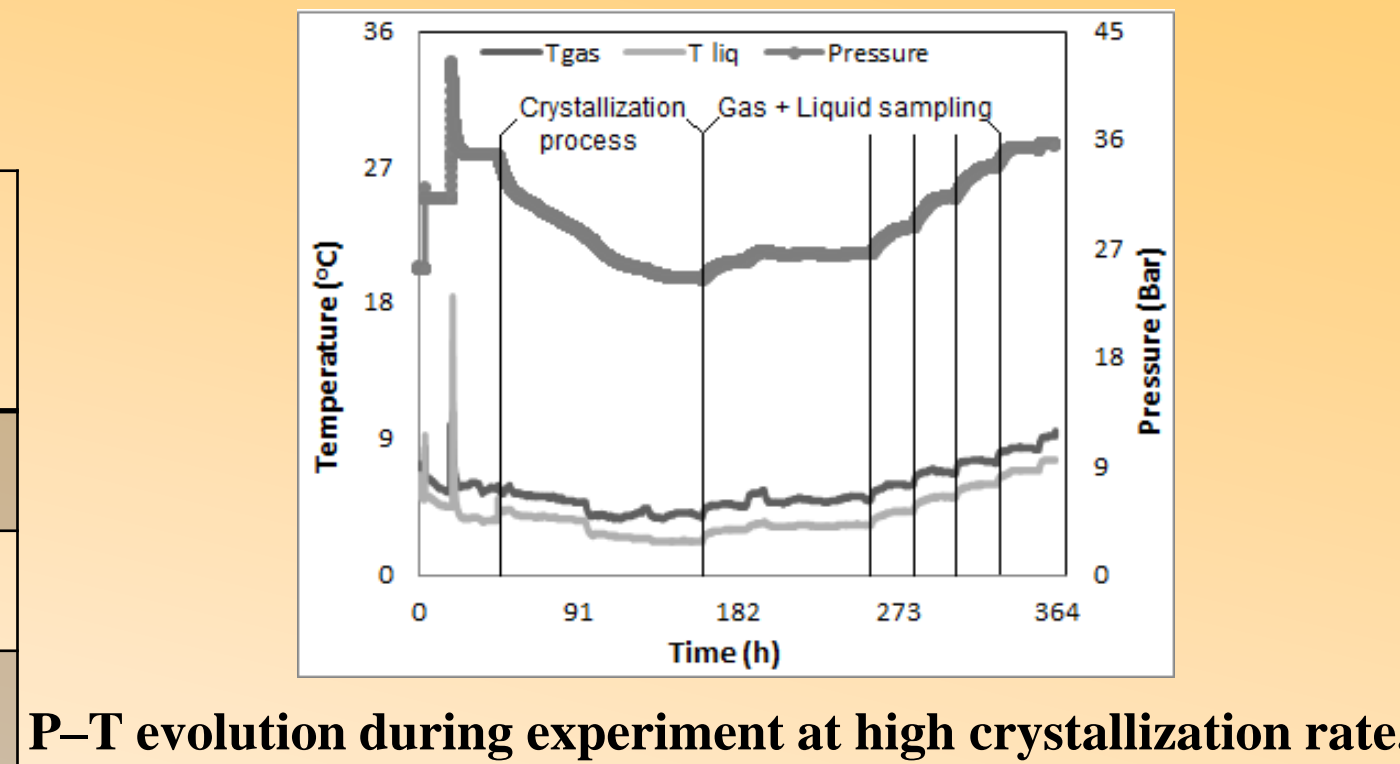


Figure 1. Experimental equilibrium data of CH₄-C₃H₈ gas hydrate at high and low driving force.

Conclusions

- Hydrate equilibria are given (T, P, gas and hydrate compositions) following two procedures.
- The two procedures used (high and low crystallization rates) highlight the kinetic effect on hydrate formation.
- The most interesting observation is the comparison between the two procedures from the same initial conditions (same pressure, temperature, mass of water and gas mixture). The Pressures are different at each equilibrium point (temperature uncertainty ±0.5 °C, pressure uncertainty ± 0.1 bar). Figure 1 illustrates these observations.