

SOLUBILITY IN

SUPERCRITICAL CH₄



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Scientific context:

Natural gas flows in **transport network** with an average pressure of 5 MPa. Then the gas is **expanded** to 0.5 MPa before entering the distribution network. For several years now, **solids deposits** formations just behind the gas expander **have been reported** [1-3].

The solid has been identified as **elemental sulfur** and its **behavior** is now **understood** thanks to a **modeling tool** [4].

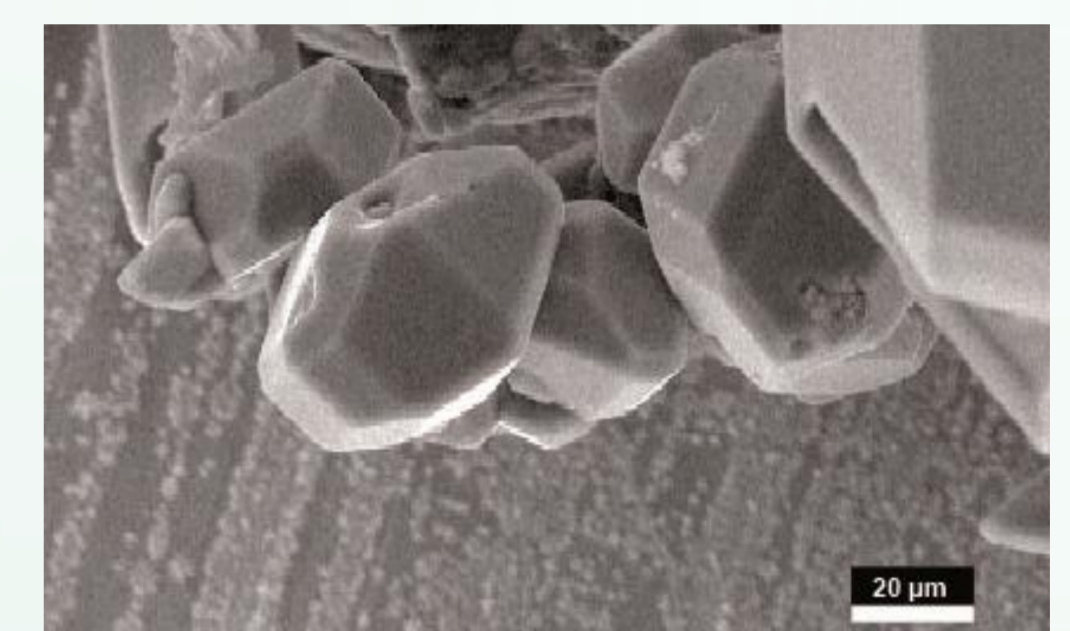
In order to **prevent** the apparition of **solid sulfur deposits** causing security and maintenance **problems** it is imperative to **determine sulfur solubility** in natural gas at transport conditions of pressure and temperature [5-7].

The **aim** of our study is to develop a **laboratory scale pilot** able to **quantify sulfur solubility** in natural gas at **transport conditions**

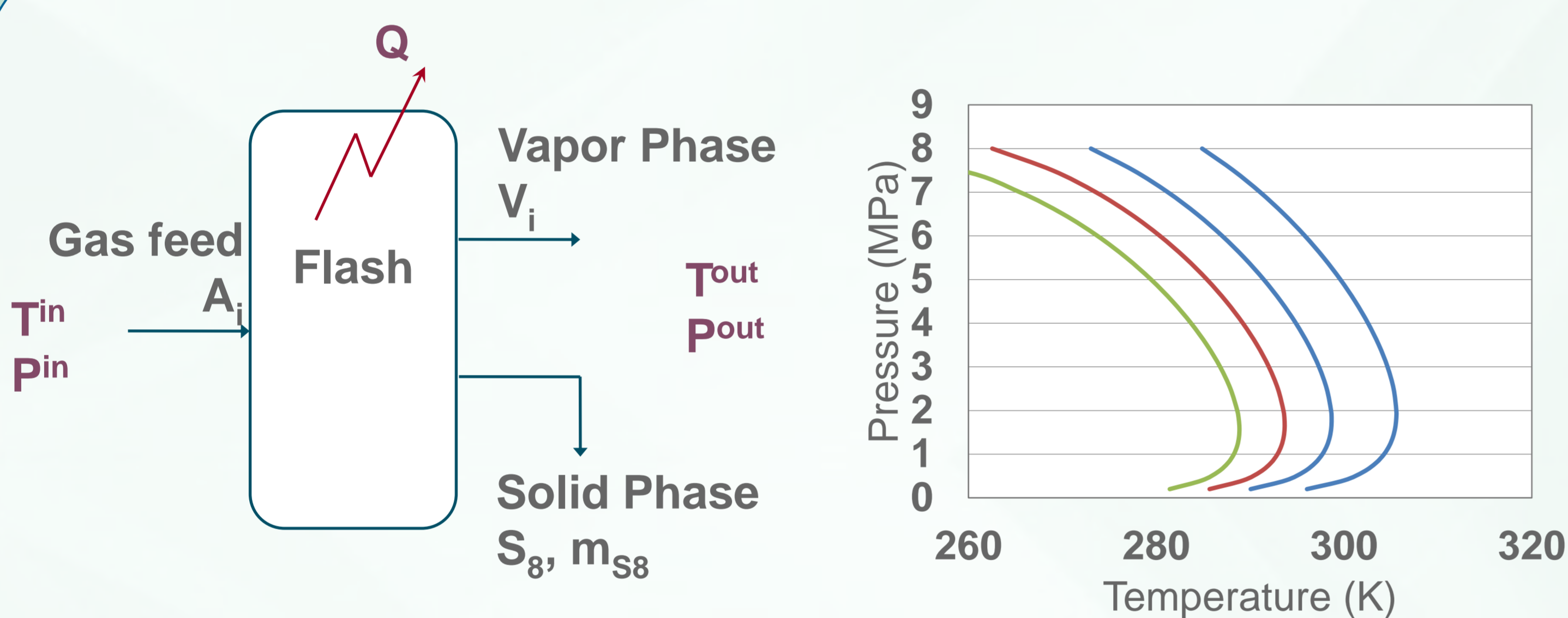
Gas expansion Facility



S8 deposit



SEM observed S8



Reactive flash diagram

Calculated isosolubility curves

Modelisation:

To **eliminate** solid sulfur deposition it is necessary to **understand** the deposit **mechanism**. 2 hypothesis have been made: **Condensate** and **desublimation**.

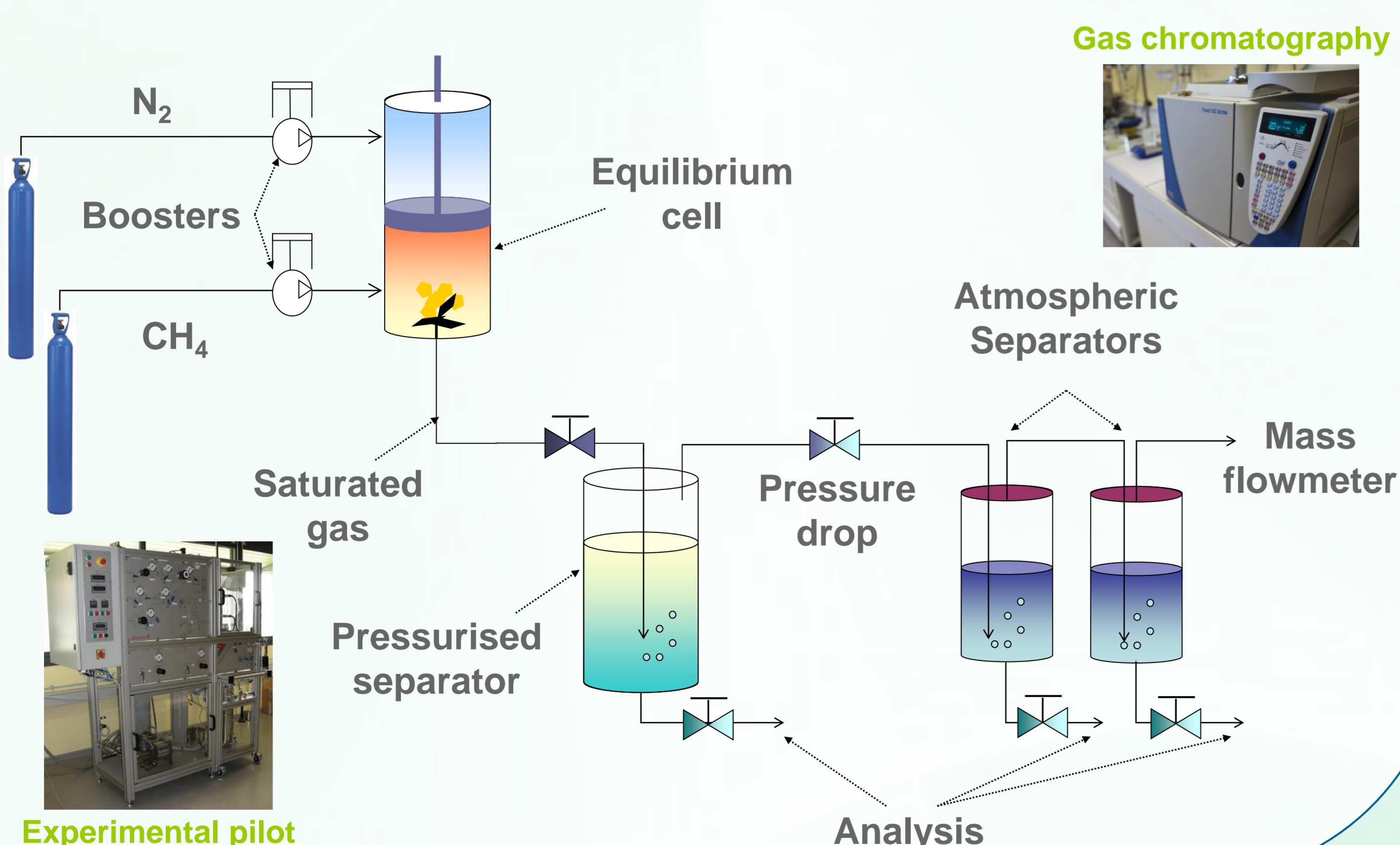
Both hypothesis have been studied thanks to a **reactive flash model** [4]. Its constitutives equations are classically the chemical and physical **equilibriums** as well as partial mass and energy **balances**.

Desublimation appears to be the most **plausible mechanism** explaining the formation of a sulfur deposit. Indeed **pressure reduction** implies **temperature reduction**, which reinforces solid formation.

Experimental pilot:

The experimental pilot **principle** can be resumed following **3 steps**:

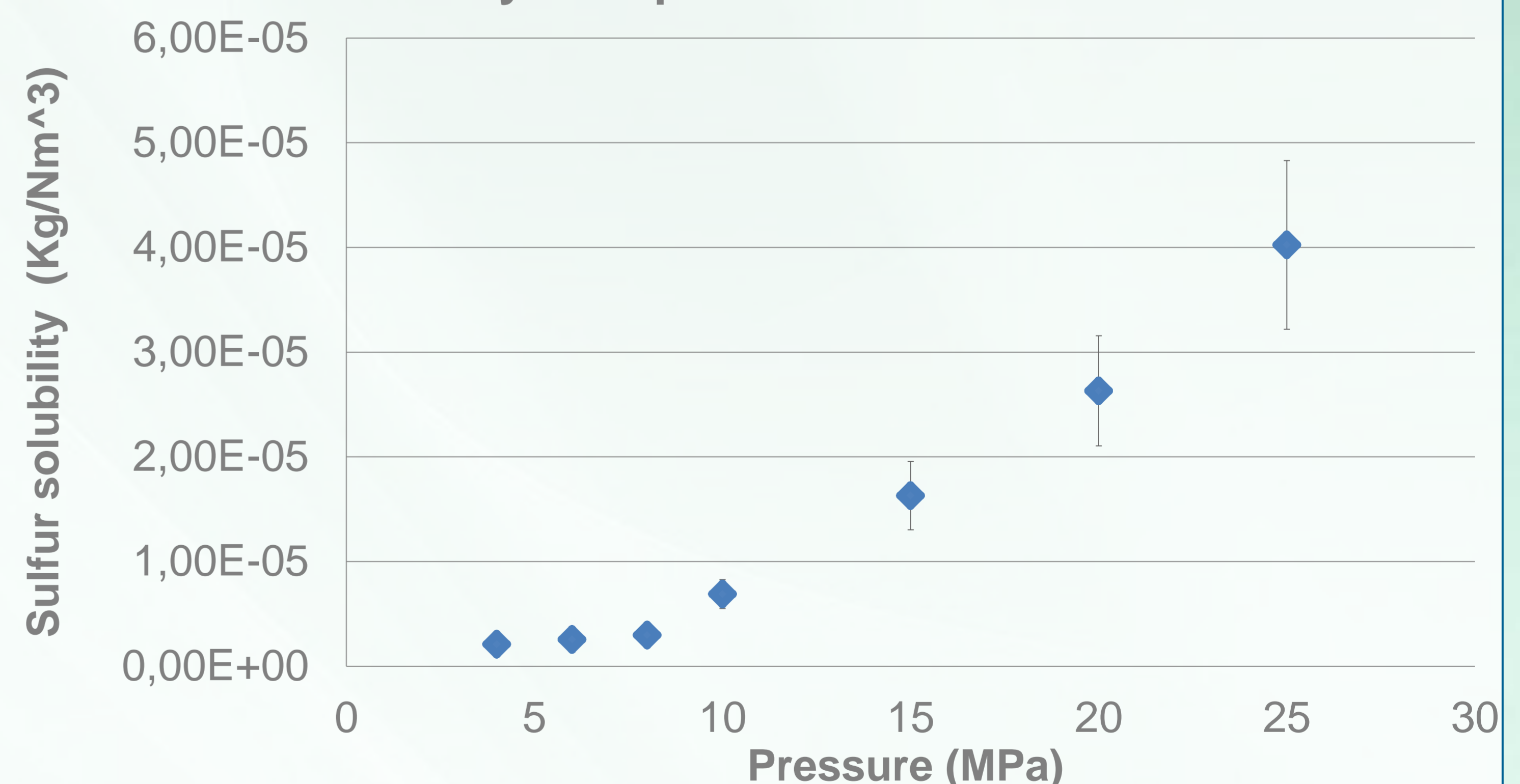
1. An equilibrium cell provides gas **saturation**. Its particularity is to keep constant the gas pressure while the gas is flowed out.
2. The dissolved sulfur is **trapped** in 3 separators placed in series thanks to **reactive absorption** solutions. The first absorption occurs **under pressure** while the 2 other take place at atmospheric pressure
3. At last, sample of the trapping solution are taken and **analysed** by **Gas chromatography** to determine **sulfur solubility**.



Experimental pilot

Results and Perspectives:

Sulfur solubility in supercritical methane at 363.15K



Sulfur solubility in supercritical CH₄ from 4 to 25 MPa, and 363.15K have been **measured** with the new experimental **device** we developed.

Our new experimental device presents several **advantages** such as **variable volume** equilibrium cell and under pressure **reactive absorption** trapping, which allows us to quantify **smaller amount** of sulfur.

Then, we are able to **measure sulfur solubility** in ranges of pressure, temperature and gas composition **not studied yet**, especially at **transport conditions**.

1. A.-B. Chesnoy, D.J. Pack. S8 threatens natural gas operations. *Oil Gas J.* April (1997), pp. 74–78.
 2. C. Wilkes, V. Pareek. Sulfur deposition in a gas turbine natural gas fuel control system. *Energy-Tech Online*. 2001.
 3. C.-Y. Sun, G.-J. Chen., Experimental and modeling studies on sulfur solubility in sour gas., *Fluid Phase Eq.*. 2003, 214, pp. 187–195.
 4. P. Cézac, J.-P. Serin, J.-M. Reneaume, J. Mercadier, G. Mouton. Elemental sulphur deposition in natural gas transmission and distribution networks. *J. Supercrit.Fluids*. 2008, 44, pp. 115–122.

5. H.T. Kennedy, D.R. Wieland., Equilibrium in the methane–carbon dioxide–hydrogen sulfide–sulfur system. *Petrol. Trans.* 1960, 219.
 6. M.-X. Gu, Q. Li, S.-Y. Zhou, W.-D. Chen, T.-M. Guo., Experimental and modeling studies on the phase behavior of high H₂S-content natural gas mixtures., *Fluid Phase Equilibria*. 1993, 82, pp. 173–182.
 7. Serin, Sophie Jay, Pierre. Cézac, François. Contamine, Jacques. Mercadier. Experimental studies of solubility of elemental sulphur in supercritical. *J. of Supercritical Fluids*. 2010, 53, pp. 12–16.