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EXPERIMENTAL STUDIES OF SOLUBILITY OF ELEMENTAL SULPHUR IN SUPERCRITICAL CARBON DIOXIDE

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INTRODUCTION

It is well known that elemental sulphur deposition is a serious problem troubling the production of sour natural gas. This deposit can also occur during transport. In the transport network, natural gas is transported at an average pressure of 5 MPa. However, to enter the distribution network, the gas pressure has to be reduced to 0.5 MPa. Consequently, a solid sulphur accumulation can occur just behind the gas expander. This solid deposit leads to a sealing problem, which regularly compromises the operation of the station. One of the hypotheses proposed to explain the solid accumulation and based on a thermodynamic approach [1] is the desublimation of sulphur. Indeed, during gas expansion, the pressure and the temperature both decrease. Consequently, the gas may become over saturated in sulphur. Because we are below the temperature of the triple point of sulphur, part of the gaseous sulphur can be transformed into solid particles. Thus, it is important to obtain the solubility data of sulphur in natural gases under 373.15 K and 20 MPa. The first step is to determine its solubility in the major gases, which constitute natural gas like CO_2 or CH_4.
Several authors measured the solubility of sulphur in pure gases, as well as in synthetic gas with composition approaching natural gas. The experiments were all carried out under conditions of temperature and pressure comparable to the conditions of field. Six groups of authors studied the solid-gas sulphur equilibrium, and determined the solubility of sulphur in natural gas Table 1 summarizes for each paper the nature of the gas considered, the ranges of pressure and temperature conditions for measuring the solubility of sulphur and the volume of the reactor used for the saturation.
Five groups of authors ([2], [4], [5], [6] and [7]) studied binary, ternary and gas mixtures of composition close to gas field composition. Kennedy and Wieland [2], Roof [3] and Gu & al. [6] studied solubility of sulphur in hydrogen sulphide. Only Kennedy and Wieland [2] and Gu & al. [6] studied solubility of sulphur in pure gases as carbon dioxide and methane, major gases in the transport network.
Kennedy and Wieland [2] studied solubility of sulphur in CO_2 and CH_4 in a temperature range from 338.71 K to 394.26 K and pressure from 6.89 MPa to 41.35 MPa. The equilibrium is established in a sulphur equilibrium bomb, which contained 18 cm^3 of elemental sulphur, maintained at the desired temperature and pressure. Equilibrium time and presence of an agitation device are not reported. The saturated gas was expanded to atmospheric pressure, and the precipitated sulphur was quantified with the ASTM Lamp Sulphur Method that consists in burning completely the sulphur trapped in glass wool, and in analyzing the products of combustion neutralized and trapped in an absorber.

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Gu & al. [6] reported the solubility data of sulphur in pure CO_2 and CH_4, with temperatures of 363.2 K and 383.2 K and pressures ranged from 12.07 MPa to 40.52 MPa for CO_2, and at 383.2 K and pressures ranged from 20.52 MPa to 50.17 MPa for CH_4. The experimental apparatus was composed of an H_2S-resistant stainless steel equilibrium cell with a piston where solid sulphur and gas contacted to establish solid-gas equilibrium. This reactor stirred by a rocking device during 20 hours was immersed in an oil bath to maintain constant temperature. A sample of saturated gas was withdrawn from the cell and flashed through a valve in a sampling tube, while the pressure in the reactor was held constant with the piston. Then, the tubing was dismantled and rinsed with 100 cm^3 of carbon disulfide to dissolve the sulphur collected. CS_2 was evaporated off under atmospheric pressure, and the sulphur was weighed.

	Gas composition	Range of temperature (K)	Range of pressure (MPa)	Volume of reactor (cm^3)
Kennedy and Wieland (1960) **[2]**	Pure CH_4, CO_2 and H_2S Binary and ternary	338.71 to 394.26	6.89 to 41.35	Not specified
Roof (1971) **[3]**	H_2S	316.48 to 383.15	7 to 31.15	355
	CS_2	338.71	7 to 34.6	
Brunner and Woll (1980) **[4]**	H_2S CH_4 - H_2S - CO_2 - N_2	373.15 to 433.15	10 to 60	400
Brunner, Place and Woll (1988) **[5]**	CH_4 - H_2S - CO_2 - N_2 - C_2H_6 - C_4H_{10}	398 to 485	6.7 to 155	30, 110 and 550
	Gas field composition	388 to 408	7 to 43	
Gu & al. (1993) **[6]**	Pure CH_4, CO_2 and H_2S	363.2 to 383.2	11.83 to 50.17	300
	Gas field composition	363.2	11.47 to 34.71	
Sun and Chen (2003) **[7]**	CH_4 - H_2S - CO_2	303.2 to 363.2	20 to 45	300

Table 1 : Summary of previous studies obtained between 1960 and 2003

The reported experimental data on the solubility of sulphur in pure major gases are far from sufficient and are in too high ranges of temperature and pressure to explain and to avoid the solid sulphur accumulation in the transport network. In this paper, solubility of elemental sulphur was measured in CO_2, with temperatures ranged from 333.15 K to 363.15 K and pressures up to 30 MPa.

MATERIALS AND METHOD

APPARATUS

The experimental apparatus shown in Figure 1 is a special design developed with Top Industrie S.A., company specializing in high pressure technology, research and design prototypes.

A stainless steel equilibrium cell where solid sulphur and CO2 contacted and established the solid-gas equilibrium is the first key of the apparatus. The equilibrium cell has a maximum working space of 500 cm3 and a maximum working pressure of 50 MPa and is equipped with a stirrer. Pure gas is introduced into the equilibrium cell using a gas booster. Another booster brings nitrogen to high pressure, and then a piston ensures the pressure regulation. A heating

band allows to reach the desired temperature in the equilibrium cell. Other parts of the apparatus include valves, manometers, pressure sensor, thermocouple, bursting discs, etc. The second key is the trapping of gaseous sulphur. A flash is made through a valve: the saturated gas was expanded to atmospheric pressure while the pressure of the equilibrium cell was held constant tanks to the piston. The saturated gas flows through two 5µm filters which trap a certain amount of solid sulphur. After, the gas bubbles into two stainless steel bottles filled with a trapping mixture. The last key is the analysis of the elemental sulphur trapped. Gas volume sampled is measured with a mass flow meter.

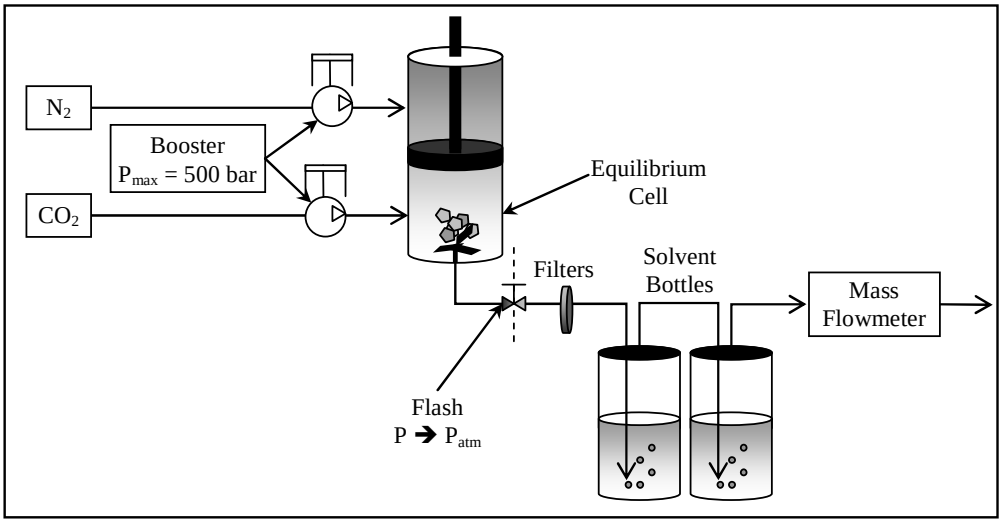

Figure 1: Apparatus for measurement of solubility of sulphur

MATERIALS

Chemicals. Sulfur is a high-purity finely dispersed solid distributed by Merck with a content of (99.0 to 100.0) %.Triphenylphosphine (TPP), triphenylphosphine sulfide (TPPS) and triphenylphosphate ($TPPO_4$) are Merck's products for synthesis and are 99 % pure each. Toluene (purity > 99.8 %) is obtained from Fisher Bioblock Scientific. Ethanol (purity > 99.5 %) is obtained from Merck.

Gases used are supplied by Air Liquide. For the pilot of saturation, Nitrogen used is an industrial gas, and Carbon Dioxide is 99 % pure. For chromatography, Helium used has a stated purity of more than 99.999 % and Hydrogen is 99.995 % pure. A mixture of 80 % of nitrogen and 20 % of oxygen is used to ignite the flame of the chromatograph detector.

Gas Chromatography. Samples are analyzed on a ThermoFisher Scientific Trace GC Ultra^{TM} gas chromatograph coupled with a flame photometric detector (FPD), which is specific for sulfur and phosphorus. Because TPPS contains a phosphorus atom, the FPD is used in phosphorus mode with a 560 nm interference filter and a base at 593.15 K. Helium is used as carrier gas at a column flow rate of $8.33 \cdot 10^{-2}$ $cm^3.s^{-1}$, the Split/Splitless Injector is operated at 573.15 K with a split ratio of 10. A TR-5 Trace GC Capillary Column with a 0.53mm internal diameter, a 1µm thick film, and a length of 30 m is used in isotherm mode at 563.15 K.

EXPERIMENTAL PROCEDURE

Saturation of gas in sulphur. Before closing the equilibrium cell, approximately 5 g of sulphur is added to it. The equilibrium cell, connected to gas cylinders, is filled with CO_2. The reactor is isolated from the rest of the apparatus, the heating band reaches the desired temperature and the stirrer establishes equilibrium between each phase. The pure gas and the solid sulphur are stirred for 15 hours to establish gas-solid equilibrium.

Flash. After equilibrium has been reached, the saturated gas is expanded to atmospheric pressure. During this step, the cell pressure is kept constant thanks to the piston. The sampling speed is controlled to be very slow to ensure maximum of sulphur deposition in filters. Then, the gas bubbles into a trapping mixture in which sulphur reacts in solution, and leave the system cleaned of sulphur. This trapping mixture is analysed by gas chromatography. The total volume of the gas withdrawn is measured using a gas meter, and then revised to standard condition.

Analysis. Filters are drying in oven at 333.15 K, and the amount of sulphur contained in filters is firstly determined by weighing with an electronic precision scale. Then, filters are dismantled and rinsed with trapping solution to dissolve the sulphur deposited and make it react. The CPG analyse of this solution ensure to get more precision. The solubility of sulphur is then calculated from the knowledge of the amount of sulphur recovered in tubing and in the two bottles, and from the knowledge of the volume of gas measured.

Principle of the Gas Chromatography Analysis. The chemical reaction developed by Bartlett and Mergurian [8] is the basis of the analytical method used in this paper. This reaction between elemental sulphur and triphenylphosphine (TPP), shown in Figure 2, leads to the formation of sulfur triphenylphosphine.

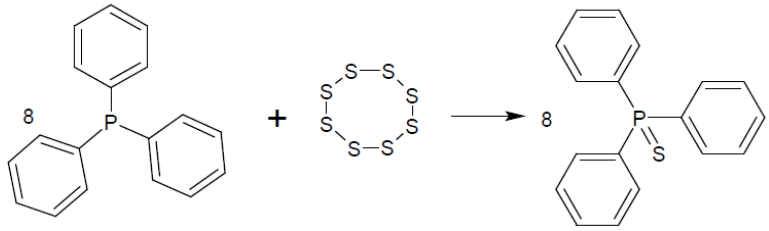

Figure 2: **Chemical reaction between elemental sulphur (S_8) and triphenylphosphine (TPP)**

So, the trapping mixture is initially constituted of toluene and an excess of triphenylphosphine (TPP). To significantly increase the efficiency of the reaction, a quantity four times higher than the stoichiometric conditions is fixed. Clark and Lesage [9] indicated that toluene was a good solvent for this reaction. Moreover, the choice of toluene as solvent has the advantage of being the same as the one chosen to clean pieces affected by sulphur deposits. When a sample of saturated gas flows through the trapping mixture, sulphur comes into contact with TPP and reacts completely in order to form triphenylphosphine sulphide (TPPS). At the end of the experiment, the analytical method developed by Lesage and Clark [9] and Davis et al. [10] is use to quantify the solution.

The product of the reaction (TPPS) is volatile and thermally stable enough to be quantified using gas chromatography. Concentration of internal standard $TPPO_4$ is fixed at 1.5 $mg \cdot dm^{-3}$. A typical chromatogram is presented in Figure 3. The four peaks generated by this analysis represent the unreacted TPP introduced in excess in the trapping solution, the internal standard $TPPO_4$ with a known concentration, the triphenyloxide (TPPO) formed by oxidation of TPP, and the product of the reaction TPPS. To ensure maximum cleanliness of the syringe,

it is flushed at least 60 times with toluene and ethanol. Pure toluene is injected to verify the cleanliness of the syringe. Each injection sample is repeated 5 times.

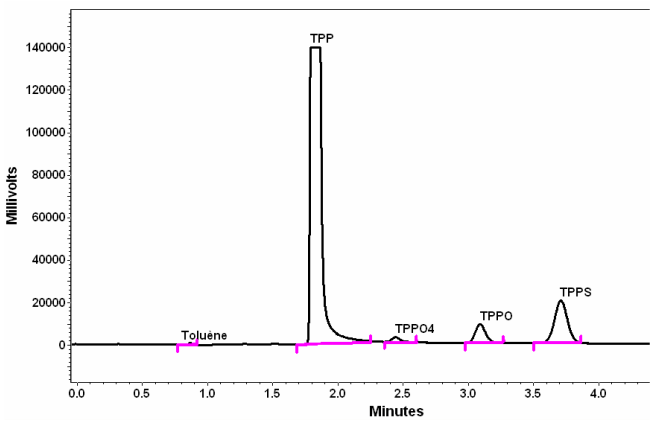

Figure 3: Order of elution and time of retention for each species in solution

RESULTS AND DISCUSSIONS

Validation of Analytical Method. First, we validated the analytical method of sulphur quantification. Samples of known concentration in sulphur are prepared. A mass of solid sulphur is weighed accurately, and non-saturated solutions are obtained by successive dilutions. TPP and $TPPO_4$ are introduced in the last diluted solution, and this one is injected in the chromatograph. The quantity of sulphur contained in the solution is determined by analytical method, and this result is compared with the known value. A deviation of 0.7 % between the theoretical weighted value and the value obtained by chromatographic analysis demonstrates the accuracy of the chromatographic method used.
A relative standard deviation consistently below 4 % is found for each analysis.

Results. Data of sulphur solubility in CO_2 up to 300 MPa, and for 333.15 K and 363.15 K have been assembled up to now. The solubility data for these two temperatures, and depending on the pressure, are given in Figure 4 for 333.15 K and in Figure 5 for 363.15 K.

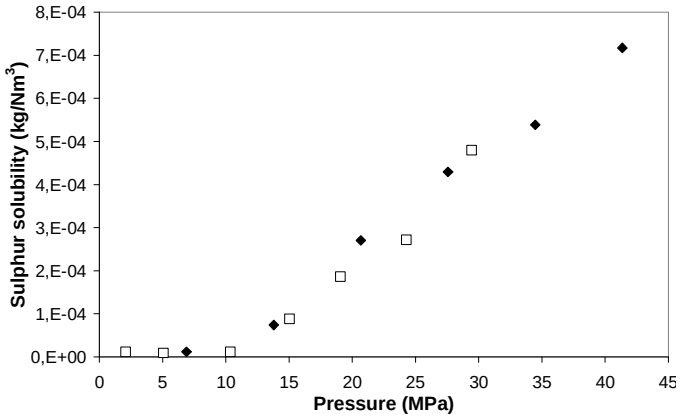

Figure 4: **Isothermal solubility of sulphur to 333.15 K depending on the pressure evolution. □, experimental data of this work; ◆, ref. [2]**

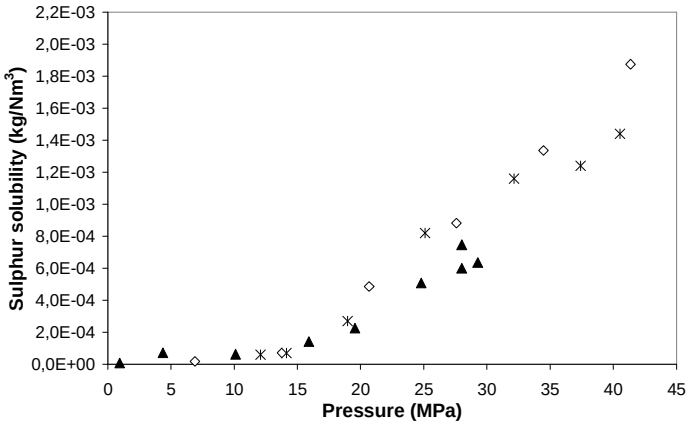

Figure 5: Isothermal solubility of sulphur to 363.15 K depending on the pressure evolution. ▲, experimental data of this work; ◇, ref. [2]; ✳, ref. [6]

CONCLUSION

The experimental apparatus used in this work was validated: new data for solubility of sulphur in CO_2 were measured. Isotherm data of the solubility of sulphur at 333.15 K are measured with pressures ranged from 2.07 MPa to 29.45 MPa. Isotherm data of the solubility of sulphur at 363.15 K are measured with pressures ranged from 0.93 MPa to 29.27 MPa.

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