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Modelling of Sulphur deposition in natural gas

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Abstract

The appearance of a solid deposit of sulphur, in the gas pressure regulation stations of the regional gas supplier Gaz du Sud-Ouest (GSO) leads to an increase in maintenance and costs. Several hypotheses have been made as to why the sulphur deposit appears. To study this phenomenon, we have modelled gas expansion by using a Flash. Not only have we modelled the phenomena, but also we have carried out an experimental procedure, which allows one to determine the mass of sulphur deposited per volume of gas. Thus, the use of these data with our model seems to prove that the hypothesis of desublimation is the right one.

Keywords: gas expansion, sulphur, deposit, modelling.

1.Introduction

Gaz du Sud Ouest supplies natural gas in southwestern France. Its network is made up of 4,200 kilometres of pipelines and 468 gas pressure regulation stations. In the transport network, natural gas is transported at an average pressure of fifty bar. However, to enter into the distribution network, the gas pressure has to be reduced to five bar. A gas pressure regulation station is used to make the pressure reduction. Gas expansion implies a decrease in temperature (the average temperature drop is 25°C). Consequently, there is an accumulation of a solid on the sound absorber (a porous cylinder), which is located just behind the gas expander (see 2 and 3 on Figure 1). This solid deposit leads to a sealing problem, which in turn compromises the operation of the station. The station has to be cleaned. Thus, the apparition of this solid leads to an increase in financial costs. The different analyses made to identify this deposit showed that it is mainly constituted of sulphur. The purpose of this paper is first of all to set up a model, which is able to predict the conditions under which the sulphur deposit appears during gas expansion. The second objective of this paper is to verify the different hypotheses, which endeavour to explain the appearance of the solid deposit.

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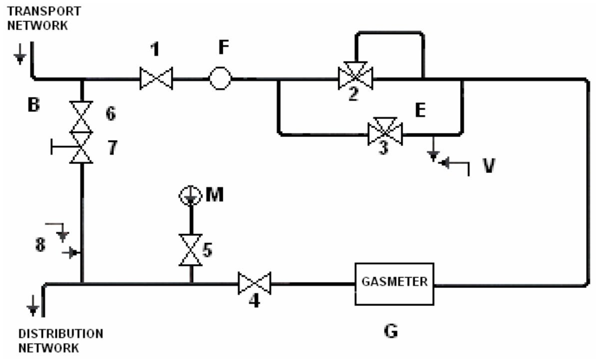

Figure 1. a gas pressure regulation station (F: filter, E: gas expansion, V: main valve, G: gasmeter, B: bypass, M: manometer).

2. Setting up the modelling of gas expansion

2.1 Equations of the model

We choose to model the gas expansion by a Flash. We consider the gas expansion of an inflow gas phase in order to obtain outflow phases (more specifically, a gas phase and possibly a solid phase). Chemical reactions can be taken into account. The model is based on the classical equations below:

- Mass balances.
- Physical equilibria: They are formulated in terms of Fugacities.

$$f_i^V(T^{out},P^{out},x_i^v) = f_i^S(T^{out},P^{out},x_i^s) \qquad i = 1, nbconst \tag{1}$$

- A energy balance

Assuming there is isenthalpic gas expansion, the sum of the outflow enthalpies is equal to the inflow enthalpy.

$$H^V(T^{in},P^{in},z_i^v) = H^S(T^{out},P^{out},x_i^s)+H^V(T^{out},P^{out},x_i^v) \tag{2}$$

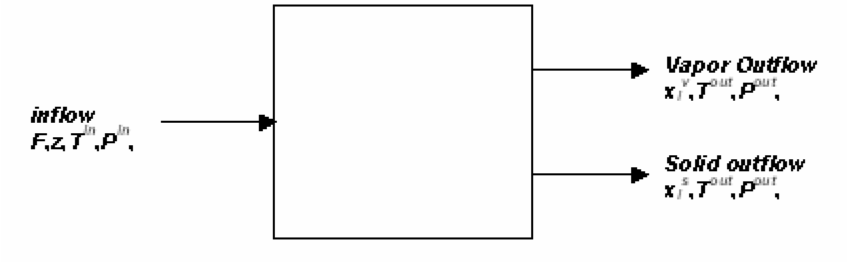

Figure2.Modelling the gas expansion by a Flash

The non-linear system obtained is solved by Newton-Raphson method.

2.2 Writing Fugacities and enthalpies

In the fluid phases (either liquid or gas), the fugacity is given by using the fugacity coefficient, while enthalpies are calculated by adding the sum of the ideal enthalpy and the residual enthalpy. To calculate these data, an equation of state is necessary. We selected the Peng Robinson equation of state, which is greatly used in the petroleum industry.

In the solid phase (considered as pure sulphur), there are two ways to express the solid fugacity of a pure compound:

- On the one hand, when using the pure sulphur gas fugacity, we have:

$$\mathrm{f}^{*S}(T,P) = \phi^{*G}(T,P^{sub}(T))\ P^{sub}(T)\exp(\frac{v^{*S}}{RT}(P-P^{sub}(T)) \tag{3}$$

Where P^{sub} is the sublimation pressure of the compound

V^{*s} is the molar volume of the pure compound.

- On the other hand, when using the pure sulphur liquid fugacity, we have:

$$\ln\frac{f^{*L}(T,Patm)}{f^{*S}(T,P)} = \frac{\Delta H^f}{RT}(\frac{1}{T}-\frac{1}{T^f}) - \frac{\Delta c_p^f}{R}\left[\ln(\frac{T}{T^f})+\frac{T^f}{T}-1)\right] + \frac{v^{*S}}{RT}(P-Patm) \tag{4}$$

Where ΔH^f is the fusion enthalpy,

Tf is the fusion temperature,

Patm is the atmospheric pressure,

Δc_p^f is the difference of the liquid and solid heat capacities under atmospheric pressure at fusion temperature. This term is an only an approximation because we don't know the liquid heat capacity when below the fusion temperature.

The liquid fugacity is calculated under atmospheric pressure because the fusion enthalpy is only known under this pressure.

The solid enthalpy is equal to the sum of the liquid enthalpy at fusion temperature, plus the fusion enthalpy, plus the integration of the solid heat capacities between the fusion temperature and the outflow temperature, plus a Poynting term, which corrects the pressure.

2.3 The Parameters of sulphur

To use the Peng Robinson equation of state, for each compound we have to determine *a* (energy parameter) and *b* (co volume). The critical temperature, the critical pressure and the acentric factor of the pure compounds are requirements and they are taken from the data bank of PROSIM©. For sulphur, the real critical data are not suitable, because around the critical point, sulphur is a mixture of several molecular species (mainly S_2), but under our conditions the main molecular specie of sulphur is S_8. Heidemann proposed correlations (eq.5) to calculate a and b for sulphur; whereas Gu et al. proposed pseudo-critical values for S_8 (eq.6).

$$\begin{aligned} a_{S8} &= 10.1835 - \frac{508.1}{T} + \frac{5896.}{T^2} \ \mathrm{Pa\,m}^6 mol^{-2} \\ b_{S8} &= 1.3122\ 10^{-4}\ \mathrm{m}^3 mol^{-1} \end{aligned} \tag{5}$$

$$\begin{aligned} \mathrm{Tc},_{S8} &= 1025\ \mathrm{K} \\ \mathrm{Pc},_{S8} &= 5.0\,\mathrm{MPa} \\ \mathrm{w}_{S8} &= 0.4439 \end{aligned} \tag{6}$$

To choose which the one that we will use, we express the fusion enthalpy as below:

$$\ln\left(\frac{f_{S8}^{*L}(T,P)}{f_{S8}^{*G}(T,P)}\right) \approx \frac{\Delta H(Tm,P)}{R}\left(\frac{1}{T} - \frac{1}{Tm}\right) \tag{7}$$

The use of the parameters of Gu only allows one to find a value close to the experimental value. However, the values obtained with Heidemann parameters have an opposite sign and a lower absolute value. So, we choose the parameters given by Gu et al. to describe sulphur's behaviour.

3. Mechanism(s) of sulphur deposition

Three hypotheses where made about the way the sulphur deposit appears.

- The first one is that the chemical reactions, which lead to the formation of sulphur, occur while gas is in expansion. Nevertheless, this hypothesis seems wrong because the velocity of the gas is very fast (about one hundred meters by second). Consequently, the reactions should be very fast too.
- Another hypothesis is that during gas expansion, the heaviest components of the gas liquefy, thus solving a part of the gaseous sulphur. Yet, after gas expansion, these components would vaporise due to the temperature increase; whereas solid sulphur appears on the walls of the pipelines. To test this hypothesis, we plot the phase envelope (Figure 3) of the main gas transported by GSO (using the main components of this gas). We find that the phase envelope is far from the operating conditions of the gas pressure regulation station (represented in Figure 3 by an arrow). According to this result, the feasibility of this hypothesis is very low.
- The last hypothesis concerns the desublimation of sulphur. During gas expansion, the pressure and the temperature decrease. Consequently, the gas could become oversaturated in sulphur. Because we are below the temperature of the triple point of sulphur, a part of the gaseous sulphur becomes solid particles.

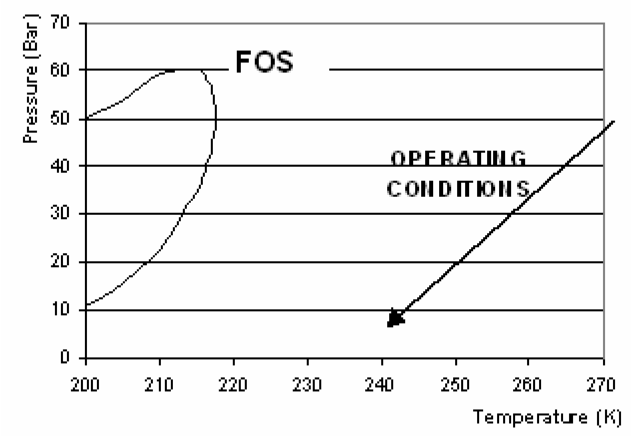

Figure 3. Phase envelope of the main gas transported by GSO.

4. An industrial case study

We ask operators of gas pressure regulation stations, when the stations had to be cleaned due to sulphur deposit. We also requested that they send us the sound absorber and give us the operating conditions of the station. Indeed, the sound absorber has the particularity of trapping all the solid particles (it acts as a filter).

Back at the laboratory, by using a crystallisation method, we determined the mass of sulphur trapped in the sound absorber. Moreover, since GSO gave us the volume of gas delivered by the station, we can determine the mass of sulphur deposited per normal cubic meter of gas (this corresponds to the values given in the “deposit” column in the following tables).

The operating conditions given by the company are the outflow temperature and pressure. The model allows one to evaluate the inflow temperature, since the calculated deposit is equal to the experimental deposit. Likewise, the inflow and the outflow solubilities are computed.

Table 1 operating conditions of different cases of gas pressure regulation stations.

	Upstream		downstream	
Case	T^{in}(°C)	P^{in}(bar)	T^{out}(°C)	P^{out}(bar)
A	24	40	7	9.8
B	33	22	9	11
C	15	48	-12	4.9
D	14	45	-12	4.3
E	19	45	-5	4.8

The amount of sulphur downstream is calculated as the sum of the outflow solubility and the deposit.

Tables 1 and 2 give the operating conditions of different cases and the corresponding calculated values.

Table 2. Calculations of solubility of sulphur (as S_8) upstream and downstream and evaluation of the amount of sulphur present in the natural gas..

Case	Solubility downstream ng.Nm^{-3}	Solubility upstream ng.Nm^{-3}	Deposit ng.Nm^{-3}	Amount of sulphur upstream ng.Nm^{-3}
A	0.45	5.12	1.69	2.14
B	0.62	3.46	0.67	1.29
C	0.03	2.25	0.95	0.99
D	0.04	1.81	0.79	0.83
E	0.11	3.27	2.44	2.55

We can see in Table 2 that in all cases the amount of sulphur in the inflow is inferior to the upstream solubility of sulphur. These results agree with the hypothesis of desublimation.

5. Conclusion

We have written a model, which is able to estimate the solubility of sulphur under standard gas transportation conditions. The study of the three hypotheses proposed to explain the appearance of sulphur deposit during gas expansion seems to show that neither the condensation of the heaviest components, nor the various chemical reactions are responsible for the deposit. The result of our model and the experimental values of the deposit tend to support the hypothesis of desublimation.

Nevertheless, if chemical reactions are not the cause of solid sulphur deposit, they can act during gas transportation, increase the amount of sulphur deposited and help the phenomena of desublimation.

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