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Water content assessment in acid gas

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ABSTRACT

Natural gas is well known as the cleanest fossil fuel. Today, it is estimated that more than 40% of the remaining conventional natural gas reserves are deemed to be acid, i.e., containing significant quantities of CO_2 and H_2S. As the global consumption of natural gas is expected to steadily grow, the demand will be met by sources such as sour/acid gas fields. In some specific applications that require cryogenic processes (LNG, NGL recovery), this issue is commonly addressed upstream of the gas dehydration unit, so that the gas is already sweet when arriving the drying section. In the other cases, the effect of the acidic species on the gas water content is often not properly accounted for, whereas an accurate appraisal of the water content is paramount for the sizing of dehydration units.

There are several methods to estimate the water content: some of them are based on empirical correlations or on thermodynamic models. This paper first explains why it is crucial to address the problem in terms of dehydration unit design and plant reliability. Herein, we will focus on CO_2 rich gas mixtures, for which a comprehensive literature review from the public domain, and discussion of mathematical methods or thermodynamic models used for water content estimation are presented. Finally, a new correlation, based on thermodynamic assumptions, was developed and was tested by comparison with experimental data obtained with a new laboratory experimental set-up. This equipment uses a Tunable Diode Laser Spectroscopy (TDLS), with an accuracy of +/- 1%.

Water content assessment in acid gas

1. INTRODUCTION

The consumption of natural gas is expected to grow steadily, and the demand will increasingly be met by sources such as sour/acid gas fields. This will have an impact on the whole gas processing chain, and especially on gas dehydration. A common example is the removal of high CO_2 content with process technologies that require preliminary drying of the gas. This imposes the accurate assessment of the influence of acid gases, in particular CO_2, on the gas water content, which today remains a challenge.

This paper first explains why it is crucial to address the problem in terms of dehydration unit design and plant reliability. A comprehensive literature review from the public domain, and discussion of mathematical methods or thermodynamic models used for water content estimation, are presented. Finally, a new correlation, based on thermodynamic assumptions was developed and was tested against experimental data obtained with a new laboratory experimental set-up.

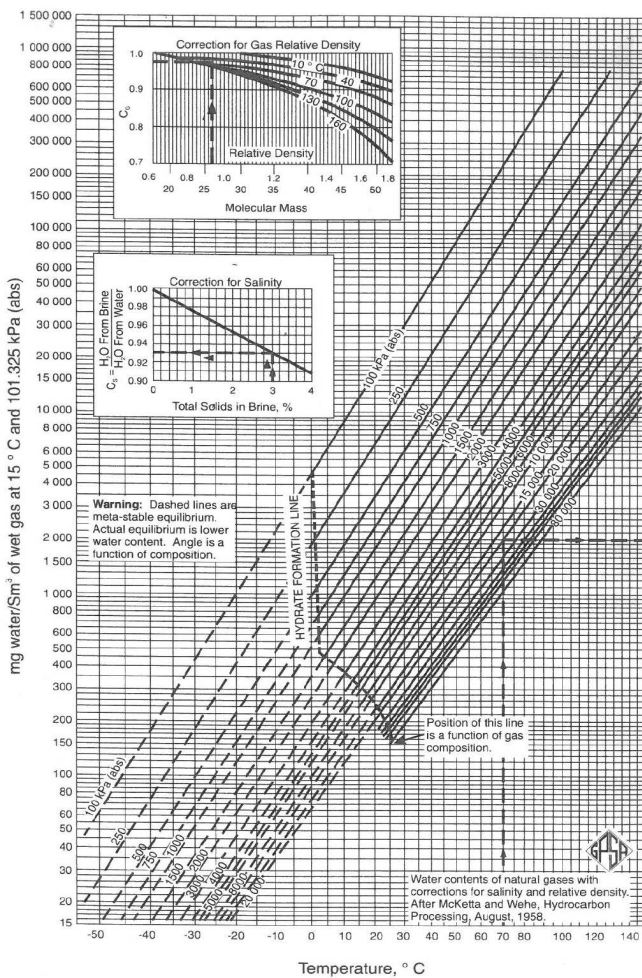## 2. WATER CONTENT : KEY PARAMETER FOR GAS DEHYDRATION UNITS

Fig. 1: McKetta-Wehe chart

Designing a natural gas dehydration unit requires an accurate estimation of the water content, that is to say the water saturation state at the operating pressure and temperature. In the case of molecular sieve units, the water content in the gas phase is one of the main sizing parameter, together with the flow-rate and the expected lifetime.

In the case of a sweet gas, the water content can be calculated by phase equilibria-based commercial softwares, or estimated using the McKetta and Wehe chart [1], (Figure 1).

The water content assessment is much more challenging when it comes to acid gas. As both pure H_2S and CO_2 contain more water at saturation than sweet natural gas, their effect on the overall water content, even when present at a few percents only, can be very significant.

Even though this aspect is well known, Process Specifications for acid gas drying sometimes minimize the real water content, or even consider the gas as a sweet gas.

Since the first role of a dehydration unit designer is to check the data, and especially the suggested water content at saturation, the problem is usually identified, and a more realistic value is calculated to serve as the basis of the design, in agreement with the client.

Several sets of experimental data and charts are available to address the subject. To this regard, the GPSA Engineering Handbooks give a good overview of the available methods.

However, and as correctly pointed out by the GPSA, most of these methods apply to a reduced range of conditions, and/or give discrete information for a limited sets of compositions. Generally speaking, the literature of the past 50 years is poor on the subject, and an accurate appraisal of the water content in acid gas is a complex issue that requires methods comparison and interpolations.

As a consequence of this, the reliability of the results is very often questionable in terms of accuracy. Therefore, to be on the safe side, dehydration unit designers may have the temptation to add some margin on the value, which of course influences the dehydration unit sizing.
In practice, in most of the cases, the problem is mainly about CO_2, with contents sometimes up to 30-50%, while the H_2S level is generally much lower, and therefore of a very limited impact compared to CO_2. This is the reason why in the following of the article we will focus on the influence of CO_2.

The following example illustrates the importance of a good estimate of the water content, and its influence on a molecular sieve dehydration unit. We will assume the gas to be treated has the following characteristics:

Flow-rate	200 000	Nm^3/hr
Pressure	60	Bara
Temperature	25	°C
Composition (mol%):		
Methane	50	%
CO_2	40	%
Ethane	8	%
Propane	2	%

Under these conditions, if the gas was considered as a sweet gas, and water content estimated by the McKetta-Wehe chart, the design of the unit would be based on **690 ppmV** water. This case will be referred to as **Case 1** in the following.

Taking into account the influence of CO_2, the real water content of the gas is in fact **770 ppmV**, that is to say close to 12% higher. This realistic scenario will be our **Case 2**.

The dehydration unit has to meet the following outlet specification:

Water content:	< 1 ppmV
Pressure drop:	< 0.35 bar (end of lifetime)
Lifetime:	> 4 years

From this very simplified Process Specification, let's see the impact of the two water contents on the unit design.

NB: *1) The following results and discussions are based on typical design methods and generally well accepted number of cycles for a lifetime (~ 1500). In reality each design case is specific and has its own constraints. Some designs have to be based on less cycles, while easier conditions can lead to close to 2000 cycles. Furthermore, the actual lifetime of a unit also depends on the reality of operation (actual flow-rate, unexpected contaminants, operational upsets, etc.)*
2) In this paper the authors do not enter the details of adsorption theory and industrial practice. Concepts such as Equilibrium Zone, Mass transfer Zone, Ageing of the adsorbents are not explained. To know more about these subjects and better understand the causes that underlie the following results, the reader is invited to consult "Molecular Sieves Contaminants: Effects, Consequences and Mitigation", A. Terrigeol, GPA Europe Annual meeting, Berlin, 2012.

Design based on Case 1, and impact of the real water content:

Case 1	(690 ppmV)
# of vessels in adsorption	1
Vessel diameter (mm)	2 900
Mole sieve quantity (kg)	11 900
Adsorption time (hrs)	12

With an inlet water content of 690 ppmV, a typical design meeting the specification would involve 2 vessels (1 in adsorption, 1 in regeneration), 11.9 metric tons of molecular sieve and 12 hours adsorption time.

If Case 2 was applied to the same design, the additional water content would lead to either one of the following scenario:

- If 12 hours adsorption time and original flow-rate were maintained, the lifetime of the unit would decrease from 4 years to only 1.5 to 2 years maximum.

- To maintain a 4 years lifetime and 12 hours adsorption time, the flow-rate would have to be decreased from 200,000 Nm^3/hr down to ~180,000 Nm^3/hr.

Design based on Case 2, with real water content:

Case 2	(770 ppmV)
# of vessels in adsorption	1
Vessel diameter (mm)	2 950
Mole sieve quantity (kg)	13 050
Adsorption time (hrs)	12

By taking into account the real water content of the acidic gas, the resulting design to allow 4 years lifetime at the nameplate flow-rate would be significantly different. It would involve a slightly larger vessel diameter, and ~10% more mole sieve.

The above example stresses the fact that a wrong water content assessment can significantly influence the operation of an existing unit. When it comes to designing a new dehydration unit, an optimized design impose to have an accurate estimate of the real water content, that is to say of the water saturation at P and T.

In the following sections, the available literature and models that, today, can help to determine water saturation in the case of rich-CO_2 natural gases will be discussed. The development of a new correlation, able to calculate accurately the water content in a wide range of operating conditions for known pressure, temperature, and gas composition will then be explained. Finally the last part will described the experimental validation of the model.

3. THERMODYNAMIC ASPECTS OF THE CH_4 CO_2 H_2O TERNARY SYSTEM

3.1.   Phases diagrams

Before studying the ternary system it is really important to understand the behavior of each binary system. Scott and van Konynenburg [2] have presented one classification of the different phase diagrams of binary systems considering only fluid phase (not solid phase).

- *CO₂+CH₄ system*

According to the previous classification, this system can be considered as type I. In the domain of the concerned temperature this system will present a critical point for temperature lower than the critical temperature of the CO_2, 304.21 K. To illustrate this point, figure 2 presents the phase diagram of this system at 270K.
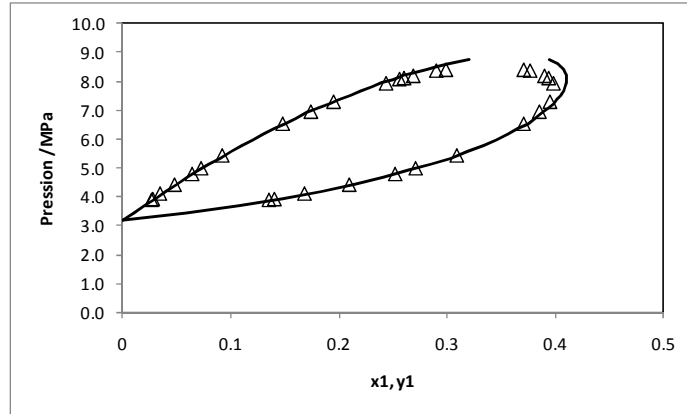

Figure 2 : Vapor liquid equilibrium of CO_2-CH_4 system at 270 K. Symbols : Webster et Kidnay experimental data [3]. Solid line corresponds to a data treatment using Peng Robinson equation of state [4].

- *CH₄ + H₂O system*

This system is considered as type III but as the melting temperature of H_2O is around 273.15 K and CH_4 is a cryogenic compound, there is no chance to have a vapour liquid liquid equilibrium. Depending on temperature, the phase diagram can present a critical point or not. Figure 2 shows the type of phase diagram we can find.
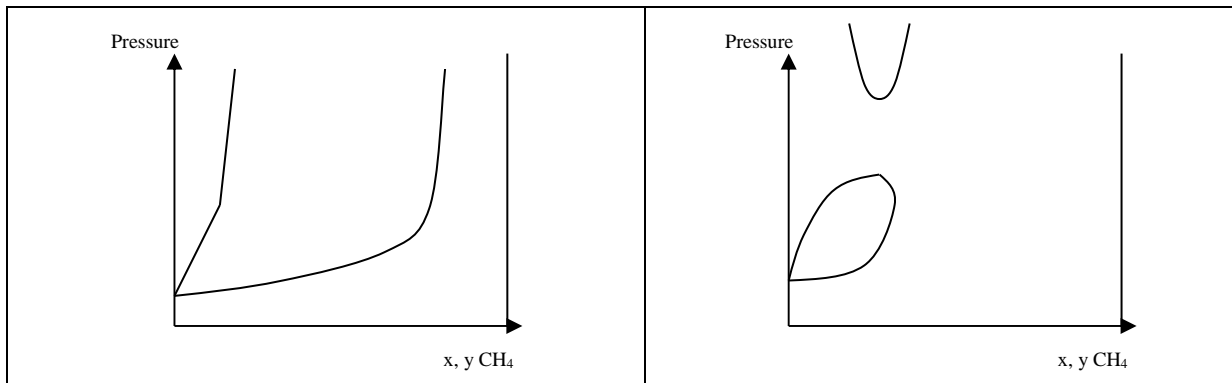

Figure 2: Phase diagram types for CH_4 + H_2O system

- *CO₂ + H₂O system*

It is the most complicated phase diagram. It is classified as type III. On the figure 3, we can observe the PT diagram. As the critical temperature of CO_2 is close to 304.21 K, the system will exhibit vapour liquid liquid equilibrium and Upper Critical End Point (UCEP). Figure 4 describes the different type of phase diagrams (PTxy) for different temperatures.
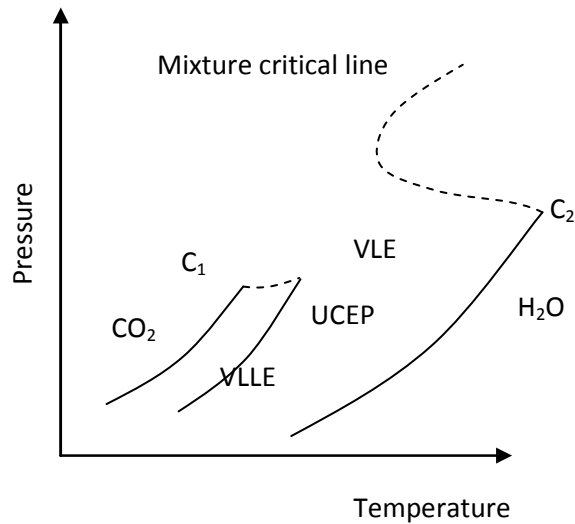
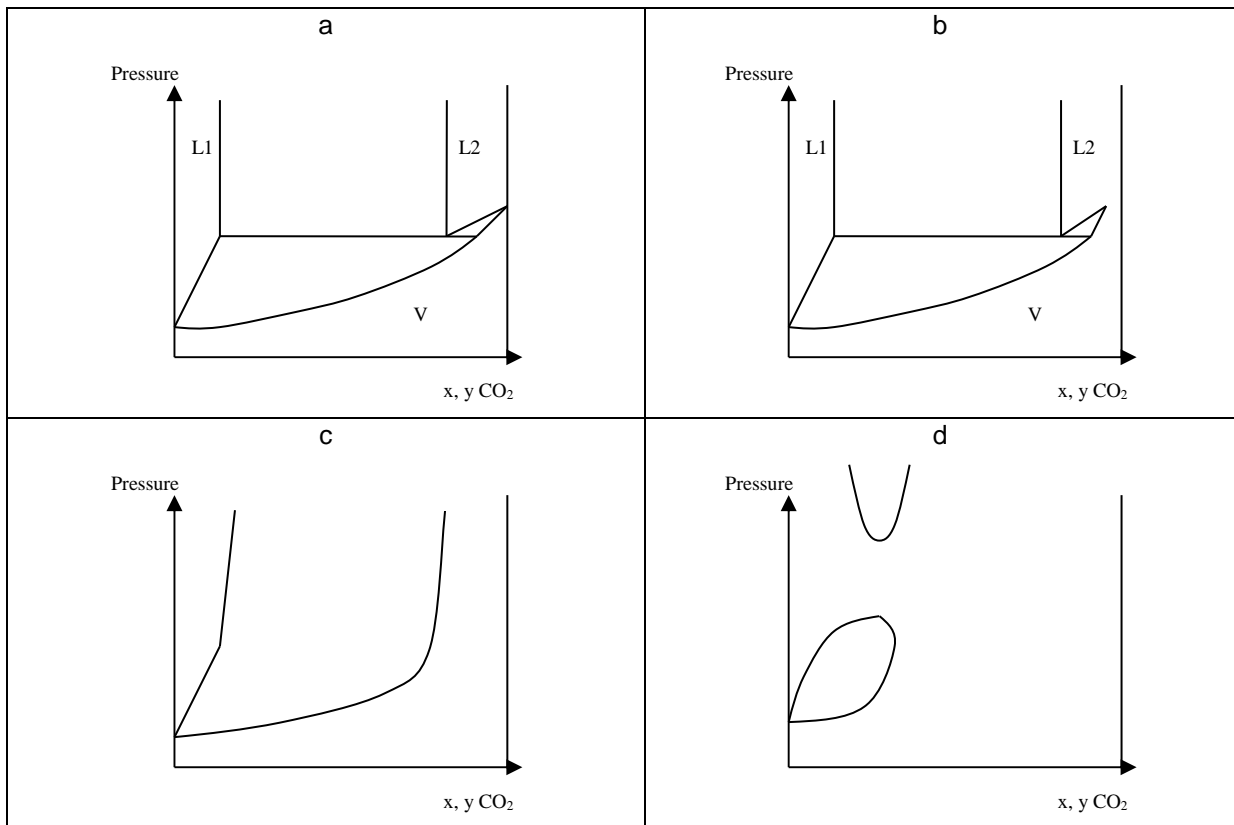Figure 3: PT diagram of CO_2 + H_2O binary system.

Figure 4: Presentation of the different types of phase diagrams of the CO_2 + H_2O binary system. a: $T < T_C$ CO_2, b: T_C $CO_2 < T < T_C$ UCEP, c: T_C UCEP $< T < T_C$ H_2O, d: T close to the T_C H_2O.

There exist numerous sets of data concerning this binary system in the open literature. But we will not use them as at high pressure (and regarding the expected concentration of CO_2 in methane stream), this system exhibits a liquid - liquid equilibrium (presence of rich CO_2 liquid phase).

3.2. Ternary system

The phase diagram of the ternary system is the combination of the phase diagram of each binary system. Qualitatively, the shape of the phase diagram changes with the temperature and the pressure (Figure 5).
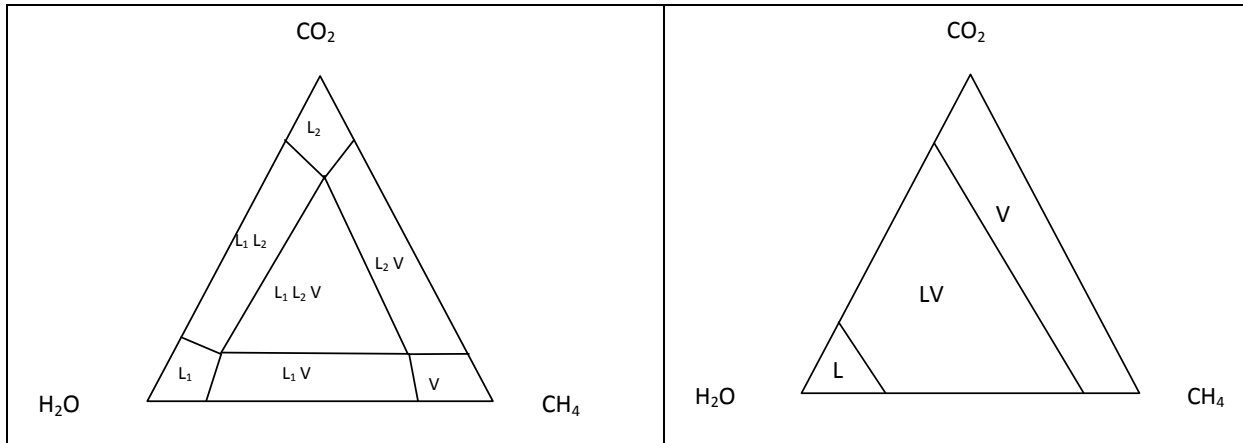

Figure 5 : Phase diagram of the ternary system. A: T and P are lower than UCEP of binary system $CO_2 + H_2O$. B: T and P are higher than UCEP of binary system $CO_2 + H_2O$.

Data on water content in the CH_4-CO_2 binary system are rather limited. Table 1 shows the existing set of data in the open literature. The work of Song and Kobyashi [5] and Sharma [6] present values of water content.

Table 1: Literature reference concerning the ternary system $CH_4 + CO_2 + H_2O$.

Song,K.Y.;Kobayashi,R., The Water Content of a CO_2-rich Gas Mixture containing 5.31 mol% Methane along the Three-Phase and Supercritical Conditions, J. Chem. Eng. Data, 35, 320-322, 1990

Dhima,A.;de Hemptinne,J.C.;Jose,J., Solubility of Hydrocarbons and CO_2 Mixtures in Water under High Pressure, Ind. Eng. Chem. Res., 38, 8, 3144-3161, 1999

Dhima,A., Solubility of natural gases in high pressure water, Thesis Univ. Claude Bernard - Lyon 1 1998

Sharma,S.C., Equilibrium Water Content of Gaseous Mixtures, Thesis The University of Oklahoma 1969

Seo,Y.T.;Lee,H., Multiple-phase hydrate equilibria of the ternary carbon dioxide, methane, and water mixtures, J. Phys. Chem. B, 105, 41, 10084-10090, 2001

Qin,J.;Rosenbauer,R.J.;Duan,Z., Experimental Measurements of Vapor-Liquid Equilibria of the $H_2O + CO_2 + CH_4$ Ternary System, J. Chem. Eng. Data, 53, 6, 1246-1249, 2008

For the water content, we can cite the work of Song and Kobyashi [5] and Sharma [6].

4. DETERMINATION OF THE WATER CONTENT

The water content corresponds to the maximum concentration of water in the vapor, gas or liquid phase at equilibrium. In Oil and Gas engineering, several authors have proposed correlations to estimate the water content. One can observe that the parameters of these correlations were determined through adjustment on experimental data. The main advantage of these correlations is that they can easily estimate the water content and do not need particular complicated algorithms and

can be implemented in spreadsheets. In this paragraph we will present a few correlations which can be used to estimate the water content (y_w).

First of all, we can consider the Raoult law $y_w = \dfrac{(1-x_g)P_W^{sat}}{P}$ which can be transformed into $y_w = \dfrac{P_W^{sat}}{P}$ if gas solubilities are negligible. P_W^{sat} is the water vapor pressure and x_g is the solubility of the gas into water. A correction term for the effect of pressure can be added $y_w = \dfrac{P_W^{sat}}{P}\exp\left(\dfrac{v_w^l\left(P-P_W^{sat}\right)}{RT}\right)$ with v_w^l the water molar volume in the same conditions of T and P.

Bukacek [7] has proposed a similar method which can be used for wet sweet natural gas.

$$y_w = 47484\frac{P_W^{sat}}{P} + B \text{ where } \log(B) = \frac{-3083.87}{491.6+t} + 6.69449 \tag{1}$$

Water content is given in lbm/MMscf and the temperature in °F. The accuracy of this correlation is around 5% between 288.15 and 511.15 K and between 1 and 960 bar. Sharma [8] and Sharma and Campbell [9] have also proposed a more sophisticated correlation which requires the estimation of fugacities of water and gas in the condition of temperature and pressure (f_W^{sat}, f_{gaz}).

$$y_w = k\left(\frac{f_W^{sat}}{f_{gaz}}\right)^Z \text{ where } k = \left(\left(\frac{P_W^{sat}}{P}\right)\left(\frac{f_W^{sat}/P_W^{sat}}{f_w/P}\right)\left(\frac{P}{P^{sat}_W}\right)\right)^{0.0049} \text{ and } Z \text{ is the compressibility factor.}$$

Behr [10] has also proposed an equation which can be used between 1.379 and 20.679 MPa.

$$y_w = \exp\left(A_0 + A_1\left(1/T\right)^2 + A_2\left(1/T\right)^3 + A_3(\ln(P)) + A_4(\ln(P))^2 + A_5(\ln(P))^3 + A_6\left(\ln(P)/T\right)^2 + A_7\left(\ln(P)/T\right)^3\right) \tag{2}$$

The parameters Ai were adjusted on experimental data (dew point).

Kazim [11] has proposed an analytical expression which can be used for sweet gas. Water content is estimated using equation 3.

$$y_w = A \times B^t \text{ where } A = \sum_{i=1}^{4} a_i\left(\frac{p-350}{600}\right)^{i-1} \text{ and } B = \sum_{i=1}^{4} b_i\left(\frac{p-350}{600}\right)^{i-1} \tag{3}$$

p is the pressure in psi, t the temperature in °F. Parameters a_i and b_i are given in Table 2.

Table 2 : Parameters of the Kazim correlation (eq. 3)..

Parameter	Range of temperature	
	T<310.93 K	310.93 K<T<355.37 K
a_1	4.34322	10.38175
a_2	1.35912	-3.41588
a_3	-6.82391	-.793877
a_4	3.95407	5.8495
b_1	1.03776	1.02674
b_2	-0.02865	-0.01235
b_3	0.04198	0.02323
b_4	-0.01945	-0.01155

McKetta et Wehe [1] have proposed a chart for the estimation of water content as shown in Figure 1 The accuracy of this chart are around 5%. This chart can only be used for sweet gas with more than 70 mol% of methane. Ning et al. [12] have proposed a correlation with 3 parameters ($y_w = \exp(a_0 + a_1 T + a_2 T^2)$).

Correction functions exist for the heavy hydrocarbons. Table 3 presents the parameters up to 100 MPa.

Table 3 : Parameter values of Ning et al. Correlation [12].

Pressure /MPa	a_0	a_1	$a_2 \times 10^{-4}$
0.1	-30.0672	0.1634	-1.7452
0.2	-27.5786	0.1435	-1.4347
0.3	-27. 8357	00.1425	-1.4216
0.4	-27.3193	0.1383	-1.3668
0.5	-26.2146	0.1309	1.2643
0.6	-25.7488	0.1261	-1.1875
0.8	-27.2133	0.1334	-1.2884
1	-26.2406	0.1268	-1.1991
1.5	-26.129	0.1237	-1.1534
2	-24.5786	0.1133	-1.0108
3	-24.7653	0.1128	-1.0113
4	-24.7175	0.1120	-1.0085
5	-26.8976	0.1232	-1.1618
6	-25.1163	0.1128	-1.0264
8	-26.0341	0.1172	-1.0912
10	-25.4407	0.1133	-1.0425
15	-22.6263	0.0973	-0.84136
20	-22.1364	0.0946	-0.81751
30	-20.4434	0.0851	-0.70353
40	-21.1259	0.0881	-0.74510
50	-20.2527	0.0834	-0.69094
60	-19.1174	0.0773	-0.61641
70	-20.5002	0.0845	-0.71151
100	-20.7974	0.0838	-0.70494

All the correlations shown above were adjusted for sweet gases. In the presence of acid gases, they have to be modified, or new ones have to be determined. For example, we can cite the abacus of Wiebe and Gaddy [13] for the estimation of water content with CO_2. Robinson et al. [14], Maddox et al. [15] and Wichert and Wichert [16] have developed some correlations to correct water content calculation from sweet gas (Figure 6).

With the presence of CO_2, water content can also be estimated from a very simple correlation, $y_w = z_{HC} y_{w\,sweet} + z_{CO2} y_{w\,CO2}$. Figure 7 illustrates an example of utilization of such correlation.

Another method consist of using semi empirical correlations: these equations start from fundamental equation of phase equilibrium and use correlation for estimating each part of the equation. Thermodynamically, these equations are inspired by classical dissymmetric approach. Liquid phase is mainly composed of water and its activity coefficient is equal to 1.

Starting from classical expression of phase equilibrium considering dissymmetric approach ($y_i \Phi_i P = \gamma_i x_i P_i^{sat} \exp\left(\dfrac{v_i^l (P - P_i^{sat})}{RT}\right)$), we obtain for water equation 4.

$$y_w = \frac{(1 - x_g) P_W^{sat}}{\Phi_w P} \exp\left(\frac{v_w^l (P - P_W^{sat})}{RT}\right) \tag{4}$$
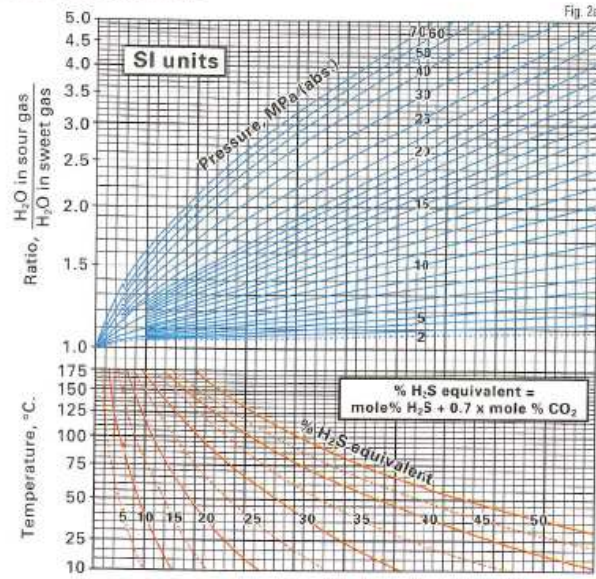
WATER-CONTENT RATIO

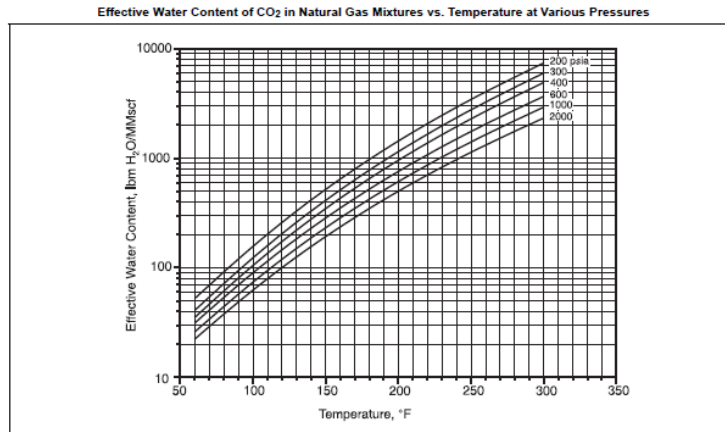Figure 6 : Chart of Wichert and Wichert, extract from [16].

Figure 7: Estimation of water content of natural gases including CO_2 (this chart is not valid for pure CO_2). Extract from GPSA handbook [17], p 20-8.

Solubility of gases are very low so $1 - x_g \approx 1$. Fugacity coefficient of water (Φ_w) is determined using a equation derived from Virial theory, $\Phi_w = \exp\left(BP + CP^2\right)$ where coefficients B and C are temperature dependant ($B = a + \dfrac{b}{T}$ and $C = c + \dfrac{d}{T}$). Constants a, b, c and d are calculated for the methane. The other terms of equation (4) are calculated using equations 5 to 8.

$$P_w^{sat} = 10^{-6} \exp\left(73.649 - \frac{7258.2}{T} - 7.3037 \ln(T) + 4.1653 \times 10^{-6} T^2\right) \tag{5}$$

$$v_w^l = \frac{18.015}{d_w}, \; d_w = \frac{62.368}{B_w}, \; B_w = \left(1 + \Delta V_{wP}\right)\left(1 + \Delta V_{wT}\right) \tag{6}$$

$$\Delta V_{wP} = -\left(3.58922 \times 10^{-7} + 1.95301 \times 10^{-9} t\right)p - \left(2.25341 \times 10^{-10} + 1.72834 \times 10^{-13} t\right)p^2 \tag{7}$$

$$\Delta V_{wT} = -1.0001 \times 10^{-2} + 1.33391 \times 10^{-4} t + 5.50654 \times 10^{-7} t^2 \tag{8}$$

Where units of T, t, p and P_w^{sat} are K, °F, psia et MPa. Table 4 gives all the parameters for the methane.

Table 4 : Values of a, b, c and d of methane in liquid water

Parameters 273.15<T<423.15 K P<22 MPa	Values (for liquid water)
a	-0.01559551
b	-1.61575838
c	0.00412617
d	-1.41158956

Accuracy of the correlation is more than 98%. Correction parameter C has to be considered if the gas contains other hydrocarbons than methane: $y_{cw} = C_\gamma y_w$.

$$C_\gamma = 1 - a_\gamma(\gamma - \gamma_M) + b_\gamma(\gamma - \gamma_M)^2 \frac{T}{T_0} + c_\gamma(\gamma - \gamma_M)^3 \left(\frac{T}{T_0}\right)^2 \qquad (9)$$

γ is the "gas gravity factor". This factor is the ratio of molar mass of the gas other the molar mass of air. For a mixture of hydrocarbons, we have $\gamma = \dfrac{\sum_i y_i MM_i}{28.97}$. γ_M is the gas gravity factor of the methane and T_0=273.15 K. If the gas contains acid gases as CO_2, another correction has to be applied.

$$y_w = C_{acid} y_{wdoux} . \quad C_{acid} = 1 - z_{H2S}^{equiv}\left(a_{acid}\frac{T}{T_0} + b_{acid}\left(\frac{T}{T_0}\right)^2 + c_{acid}\frac{P}{P_0} + d_{acid}\left(\frac{P}{P_0}\right)^2\right) \qquad (10)$$

Where $z_{H2S}^{equiv} = z_{H2S} + 0.75 z_{CO2}$. Table 5 gives the parameters of equations 9 and 10. This method is fully described by Chapoy [18].

Table 5 : Constant parameter values.

Parameters	Values
a_γ	-0.013359
b_γ	-0.091676
c_γ	0.04253
a_{acid}	0.931524
b_{acid}	-0.774631
c_{acid}	0.070257
d_{acid}	-0.000685

This correlation can be used only if the concentration of CO_2 is limited. High content of CO_2 leads to an increase of the water content with pressure (at constant temperature). For example, the figure 8 extracted from GPSA Handbook [17] presents the evolution of the water content for a gas mixture composed with 94.69% of CO_2 and 5.31% of CH_4 at 311.15K.
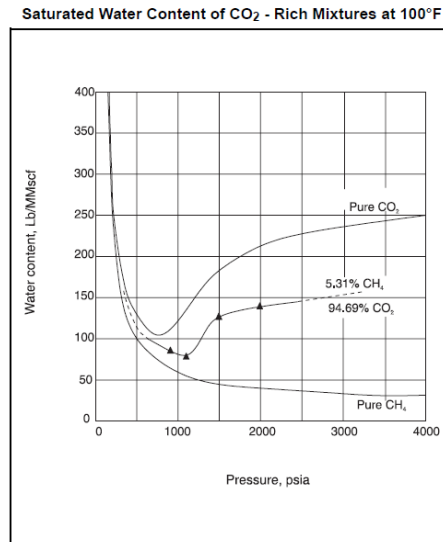
Figure 8 : Extract from GPSA Handbook [17] p 20-7 (gas mixture composed with CH_4 and CO_2 (0.9469/0.531 mol frac, from Song and Kobayashi [19])

In order to have a better prediction of the water content we have adjusted parameters based on literature data. The data of Chapoy et al. [20] on the water content of pure methane were used to fit the parameters of the correlation. Table 6 presents the new parameters. Maximum relative deviation is less than 15%. Concerning the comparison with the data of Sinayavska et al. [21], maximum deviation is close to 40% for the low temperature (around 300 K).

Using these new parameters we have predicted the data of Song and Kobayashi and Sharma. The deviations are very important (AAD=48% for the data of Song and Kobayashi and, 10% with the data of Sharma). These results seem indicating that the data of Song and Kobayashi are suspicious. The parameters of the correlation on the correction due to the presence of acid gases were adjusted on the data of Sharma. The new parameters are presented on Table 7.

Because of the lack of data for the adjustment of the parameters, we have decided to adopt another strategy which consists of using an equation of state adapted to the system with associating fluid like water.

Table 6: New values of a, b,c and d for methane with water.

Parameters $273.15<T<423.15$ K $P<22$ MPa	Parameter Values
a	0.19124865
b	-74.1600149
c	-0.00526282
d	1.83449045

Table 7: New parameters concerning the acid gases correction.

Parameters	Values
a_{acid}	0.931524
b_{acid}	-0.774631
c_{acid}	0.070257
d_{acid}	-0.000685

5. PREDICTION USING CPA EoS

Instead of using correlation with numerous parameters, another solution consists of using an equation of state. The Peng Robinson or Soave-Redlich-Kwong [22] EoSs are commonly used in oil and gas engineering. However, for substances that have the ability to form strong associating bonding interactions between molecules, like hydrogen bonding, predictions using these EoS are usually not good and it is preferable to use an equation that can take into account the association between molecules like the CPA equation of state [24]. A detailed description of the CPA-EoS and the original thermodynamic framework used in this work can be found elsewhere (Haghighi et al. [24]). In summary, the thermodynamic model is based on the uniformity of fugacity of each component throughout all the phases. The CPA-EoS is used to determine the component fugacities in fluid phases. The model can predict accurately the distribution of water in the CO_2 or CH_4 rich phase and solubility of CO_2 or CH_4 in the aqueous phase below and above the critical point of pure CO_2 as shown in Figure 9.

Hajiw et al. [25] have shown that for the prediction of the water content, no binary interaction parameter is necessary. Consequently we have used the previously described model for the prediction of water content of CO_2 + CH_4 system with no k_{ij}. Figure 10 presents some results for different concentration of CO_2.
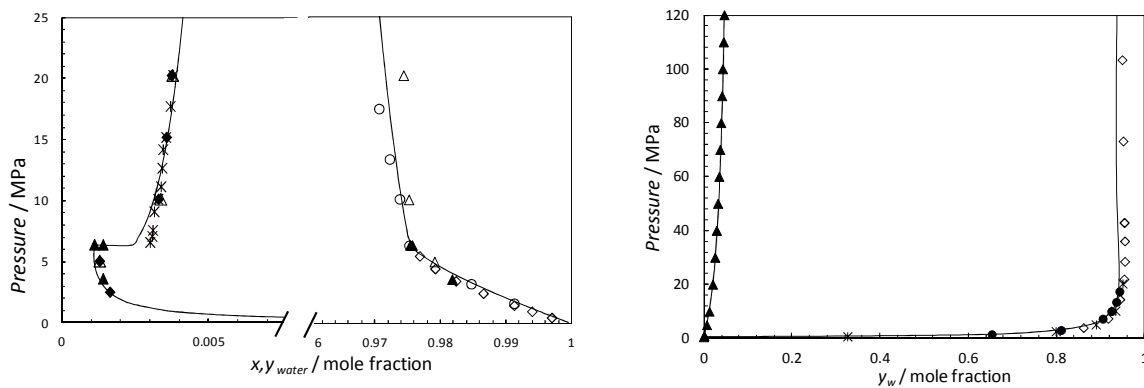

Figure 9 *Pxy*, Phase equilibria in the carbon dioxide + water system at 298.15 K left) and 423.15 K (right). Black Lines: Model predictions. Left figure: (◆) Experimental data from Wiebe and Gaddy (1941); (△) Experimental data from Gillepsie and Wilson (1982) ; (▲) Experimental data from Nakayama et al. (1987) ; (⋆) Experimental data from King et al. (1992) ; (○): Experimental data from Hou et al. (2013) ; (◇): Experimental data from Valtz et al. (2004). Right figure: (◆): Experimental data from Takenouchi and Kennedy (1964); (⋆) Experimental data from Gillepsie and Wilson (1982); (◇): Experimental data from Tabasinejad et al. (2011) at 422.98 K ;(●): Experimental data from Hou et al. (2013). (▲): calculated data Duan and Sun (2003)
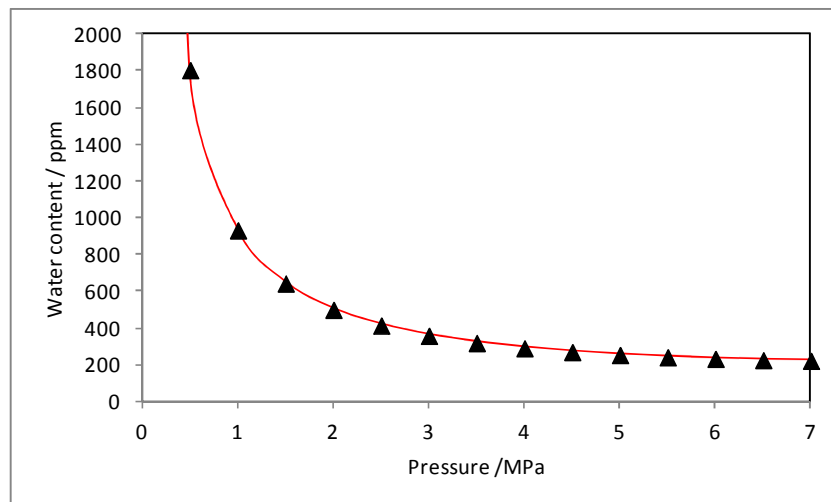

Figure 10: Water content for the 50 mole% CO_2 + 50 mole% CH_4 system as a function of pressure at 278.15 K. Red line: modified correlation, symbol: CPA model prediction with no binary interaction parameter.

Using the predicted data, and taking into account that with high concentration of CO_2 at high pressure the water increase, we have decided to modify the correlation presented in section 4 (DETERMINATION OF WATER CONTENT). The equivalent acid gas concentration is estimated using the new equation 11.

$$z_{H2S}^{equiv} = z_{H2S} + 0.75 z_{CO2} \exp\left(aP^2 + bP + c\sqrt{T}\right) \tag{11}$$

The Table 8 presents the final values of the correlation parameters directly adjusted on the predicted data. In order to validate the prediction, new experimental data were measured.

Table 8: Parameters used for the modified correlation

Parameters	Values
Equation 11	
a	-0.09791553
b	0.01977949
c	-0.00063166
Equation 10	
a_{acid}	0.28291607
b_{acid}	-0.27350135
c_{acid}	-0.01053736
d_{acid}	3.0838E-07
Equation 9	
a_γ	-0.013359
b_γ	-0.091676
c_γ	0.04253

The range of utilization of the new correlation is so far limited to 278 K < T < 313 K and P < 7 MPa

6. NEW EXPERIMENTAL DATA

In order to validate the prediction of the new correlation, new experimental data were measured. The core of the equipment for water content measurement has been originally described by Chapoy et al. [26] and Burgass et al. (2014) [27].The setup comprises of a twin equilibrium cells and a device for measuring the water content of equilibrated fluids passed from the cell. The twin equilibrium cell consisted of 2 piston-type variable volume (maximum effective volume of 300 ml), titanium cylindrical pressure vessel held within a single cooling jacket (Figure 11). Cell volume, hence pressure, can be adjusted by injecting/withdrawal of hydraulic liquid behind the moving piston. The rig has a working temperature range of 203.15 to 453.15 K, with a maximum operating pressure of 70 MPa. The moisture/water content measurement set-up consists of a heated line, a Tuneable Diode Laser Adsorption Spectroscopy (TDLAS) from Yokogawa and a flow meter. The estimated experimental accuracy of water content is ±5 ppm mole.
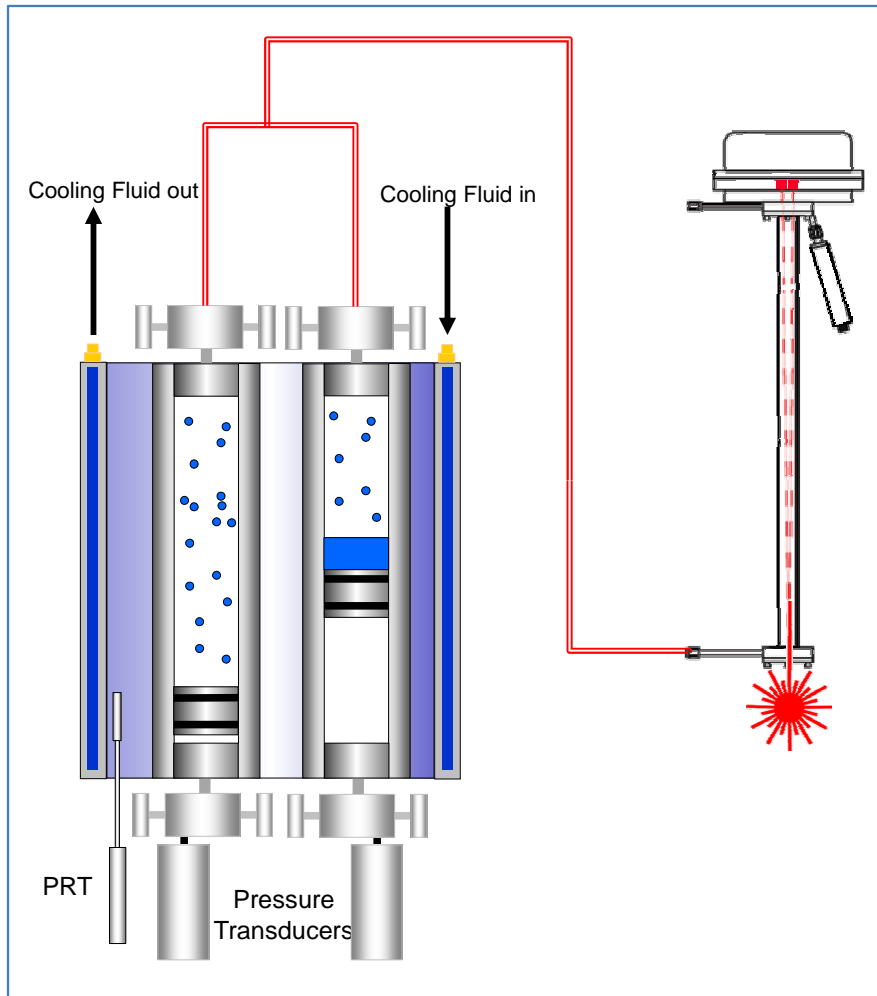
Figure 11 : Schematic diagram showing equilibrium cell and water content measurement set-up.

Table 9: show the comparison of the results with the new correlation and prediction using CPA.

Table 9. Experimental and predicted water content measurements for the three gas mixtures at the different test conditions.

Mole% CO_2	Mole% CH_4	T/°C ±0.1	Pressure Bara ±0.3	Water content ppm mole ±1%	Water content (CPA-SRK)	Water content (Correlation)
50	50	20.0	30.0	989	962	960.1
			60.0	636	600	598.9
		40.0	30.0	2961	2993	2919.0
			60.0	1791	1793	1755.0
30	70	20.0	30.0	959	928	923.5
			60.0	584	553	552.2
		40.0	30.0	2873	2878	2800.3
			60.0	1693	1661	1613.8
10	90	20.0	30.0	884	892	886.9
			60.0	502	511	505.6
		40.0	30.0	2806	2762	2681.6
			60.0	1543	1537	1472.5
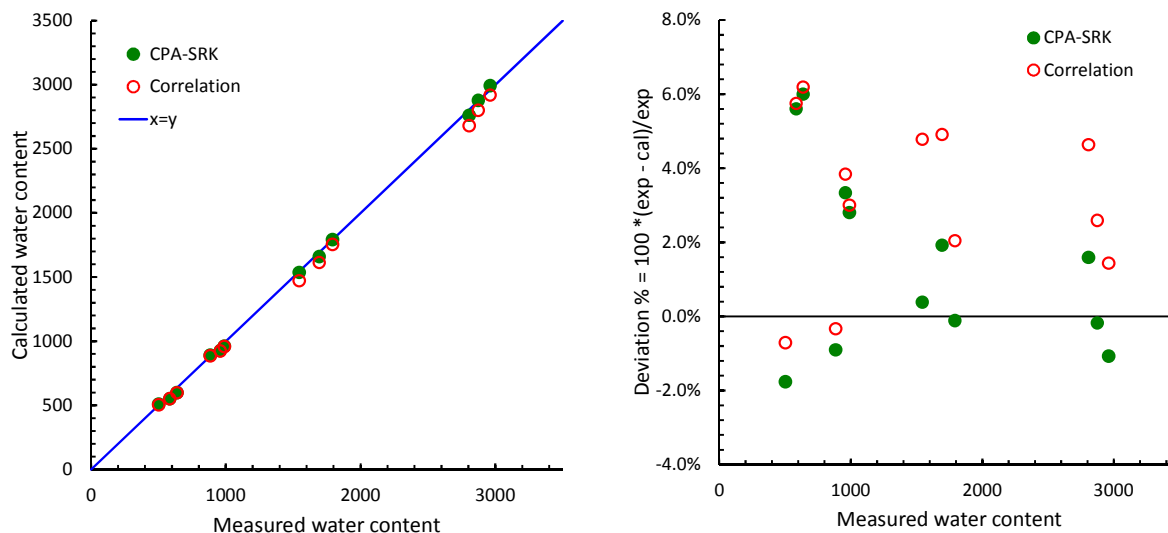
Figure 12: Comparison between experimental water content (n ppm mole), model predictions and correlation

As can be seen in Figure 12, there is an excellent agreement between the experimental data and correlation or the model. The model is slightly more accurate (AAD=2.1%) than the correlation (AAD=3.4%).

The experimental data follow the expected trends, i.e.:

- The water content is increasing with temperature at a given pressure (see Figures 13, 15 & 17)
- The water content is decreasing with pressure at a given temperature (see Figures 14, 16 & 18)
- The water content is increasing with the CO_2 concentration in the feed gas (Figures 19 & 20).
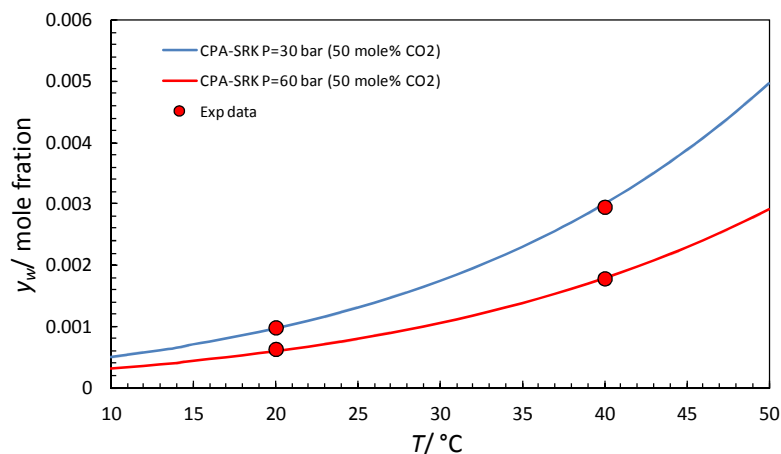
Figure 13. Predicted and experimental water content for the 50 mole% CO_2 + 50 mole CH_4 system – Temperature dependency
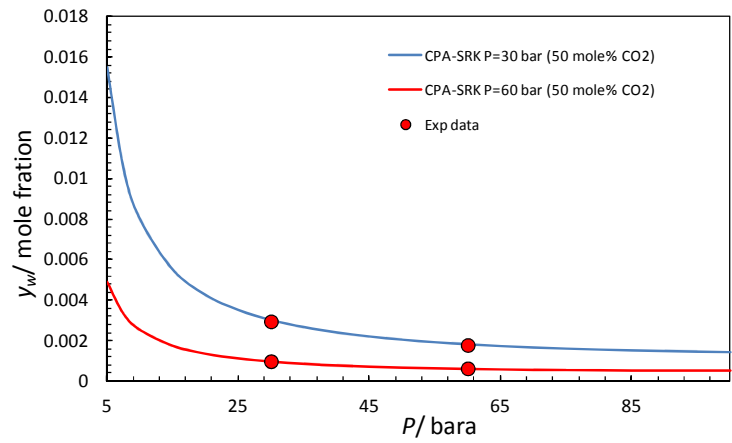
Figure 14: Predicted and experimental water content for the 50 mole% CO_2 + 50 mole CH_4 system – Pressure dependency
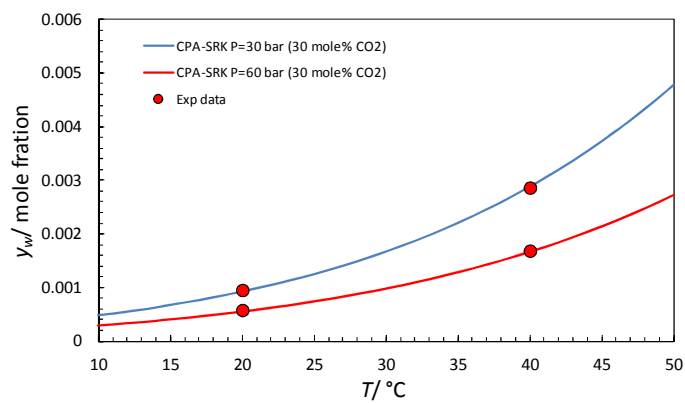

Figure 15: Predicted and experimental water content for the 30 mole% CO_2 + 70 mole CH_4 system – Temperature dependency
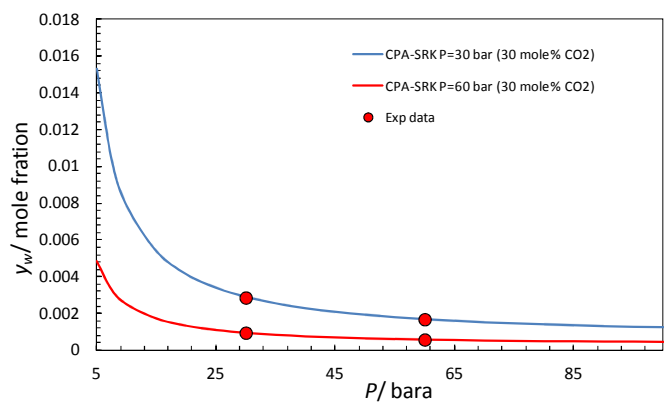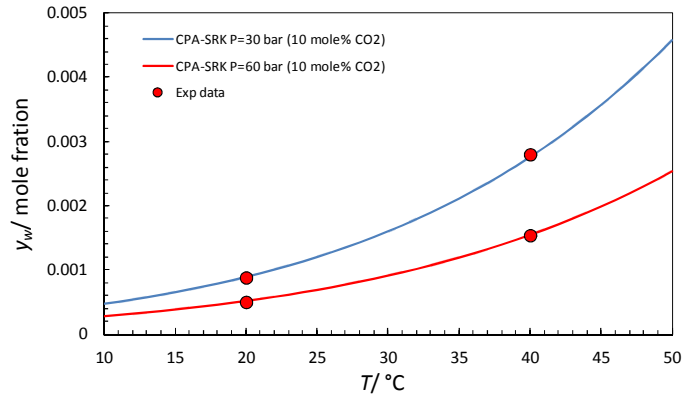

Figure 16: Predicted and experimental water content for the 30 mole% CO_2 + 70 mole CH_4 system – Pressure dependency

Figure 17: Predicted and experimental water content for the 10 mole% CO_2 + 90 mole CH_4 system – Temperature dependency
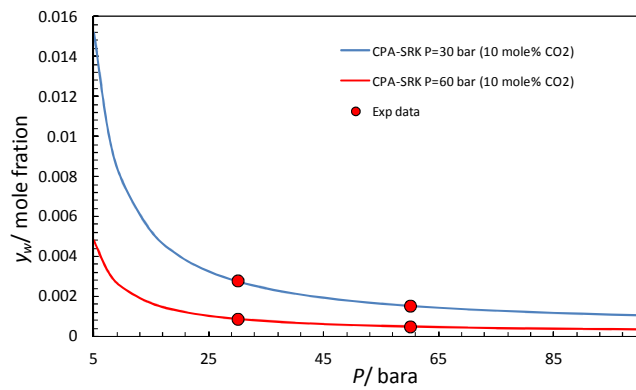

Figure 18: Predicted and experimental water content for the 10 mole% CO_2 + 90 mole CH_4 system – Pressure dependency
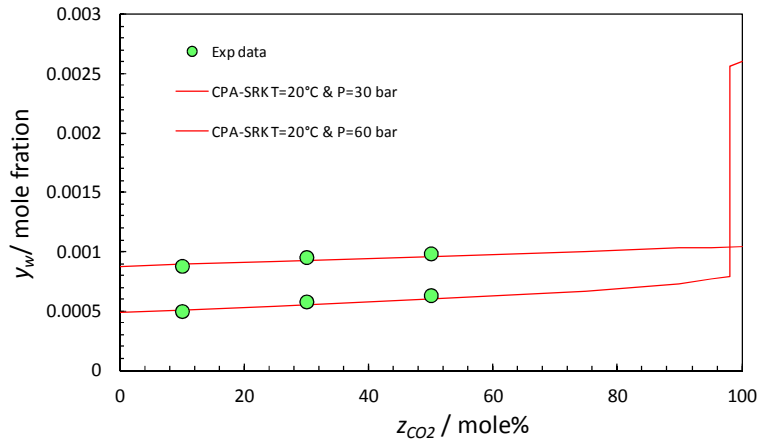

Figure 19: Predicted and experimental water content at 20°C – Effect of CO_2 in feed gas
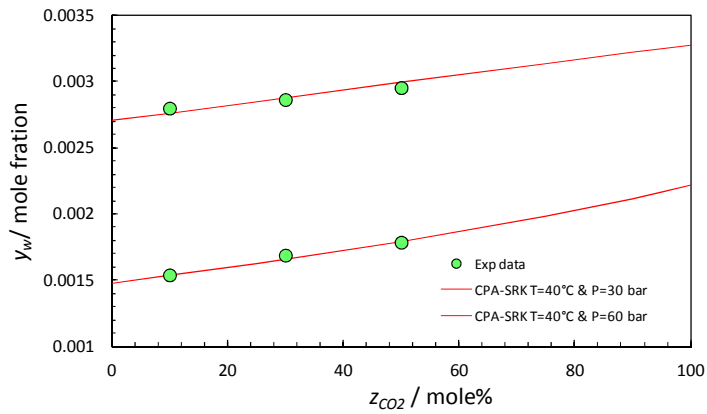
Figure 20: Predicted and experimental water content at 20°C – Effect of CO_2 in feed gas

CONCLUSION

New data concerning the measurement of water content of various mixtures composed of CO_2 and CH_4 were determined with an accuracy of +/- 1%. These new data were used to validate the predictions of a new correlation especially developed for the estimation of water content of such gas mixture. This new correlation was developed taking into account the specificity of the phase diagram of the ternary system H_2O – CH_4 – CO_2. At high pressure and with high concentration of CO_2, the water content trends to increase due to the presence of a CO_2 rich liquid phase. For this main reason, the range of utilization of the correlation is limited to 278 K < T < 313 K and P < 7 MPa. This new correlation represents with high accuracy the literature data and the new experimental data. Moreover, this new correlation gives similar results in comparison with the calculations obtained from equation of state like SRK – CPA. Therefore this correlation can be used for industrial purpose.

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