RELIABILITY OF WATER CONTENT DATA FOR NATURAL GAS-HYDRATE SYSTEMS USING SEMI-EMPIRICAL CORRELATIONS

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ABSTRACT

Water in natural gas can result in various operational problems, which may lead to equipment failure and plant shutdown. Knowing the amount of water capable of condensing from natural gas is essential. Many methods have been developed for ascertaining the amount of this condensable water (water content) from many gas mixtures. However, when hydrates are present, available methods for estimating the amount of condensable water are scarce and very limited in the open literature. The reliability of the data has always been a cause for concern due to the tendency for the inaccuracy of the results. In this study, two semi-empirical methods for ascertaining the amount of condensable water in natural gas with and without hydrates were used to test the reliability of the water content data of four different published natural gas-hydrate systems, including methane and propane gas mixture, raw/unprocessed, binary (methane + water), and synthetic natural gas. The results showed that only the data set for the methane and propane gas mixture was a reliable gas-hydrate equilibrium system, while the synthetic gas mixture needed further validation. Therefore, the methodology in this study can be used as a quick and simple means for ascertaining the reliability of water content data of natural gas-hydrate systems.

Keywords: Natural gas, water content, gas-hydrate equilibrium, semi-empirical correlations.

INTRODUCTION

Natural gas always contains water since it is produced from reservoir rocks saturated with water at reservoir conditions. Hence natural gas is always laden with water as it flows from the reservoirs through the wells, flow lines, and other surface production equipment. If not adequately handled, two-phase problems can occur, resulting in water condensation. Water in natural gas can result in numerous flow assurance problems, gas calorific value reduction, and piping and equipment corrosion [1], which may lead to equipment failure and plant shutdown. Determining the water content, or the amount of equilibrium water contained in the gas at a given temperature and pressure is imperative for the efficient design of natural gas dehydration facilities, required to effectively control the water content of the gas and thus prevent or minimize the associated operational problems. Natural gas can be in equilibrium with water or gas hydrates/ice (when hydrates

or ice has been formed in the system). In any case, the accurate determination of the water content of the gas is critical.

There are various methods of ascertaining the amount of condensable water for natural gas mixtures. While some methods use water measurement equipment directly, others use indirect means like charts and models. Reliable and available data for natural gas in equilibrium with water has led to the development of charts and correlations in determining water content. Many charts [2, 3] and correlations [4–7] provide reasonable estimates of natural gas water contents. These charts and correlations are reliable, simple, and relatively accurate. Hence, their use is still prevalent in the oil and gas industry.

Most of the data are for determining condensable water quantities for gas mixtures without hydrates at moderate to high temperatures. However, there are instances where natural gas can be in equilibrium with hydrates (usually at low temperatures and high pressures) as long as hydrate crystals exist. In such cases, methods of ascertaining the amount of condensable water are very rare [8, 9]. Where they exist, the reliability and adequacy of the data are often questionable due to the difficulty in measuring water content at low temperatures. This difficulty and lack of accuracy emanate from the fact that the metastable liquid water often extends well into the gas hydrate region, and a large quantity of gas is usually required to be in equilibrium with the hydrates, making measurements difficult [10, 11]. Another reason is that the amount of condensable water is typically minimal. Hence, difficult to measure compared to gas mixtures where hydrates are absent.

Published method(s) for screening and selecting accurate data of natural gas mixtures in equilibrium with hydrates are very rare. The accuracy of the water content data of this type of natural gas system is paramount in mitigating the operational problems associated with condensable water within the entire natural gas value chain. Therefore, this study aims to ascertain the reliability of the water content data set for natural gas – hydrates systems using two semi-empirical correlations.

SEMI-EMPIRICAL CORRELATIONS

For this study, two semi-empirical models for calculating the amount of condensable water of natural gas mixtures with and without hydrates are used for the reliability tests. The models are discussed in the next section.

Mohammadi et al. [12] Correlation

Mohammadi et al. [12] developed a semi-empirical correlation based on the uniformity of fugacities of each component throughout all the phases for estimating the amount of condensable water in natural gas mixtures without hydrates. They showed that the mole fraction of water in the gas phase could be evaluated using the following equation.

$$y_w = \frac{p_w^{sat}}{\phi_w^g p} \exp\left(\frac{v_w^l \left(p - p_w^{sat}\right)}{RT} \right) \tag{1}$$

where:

y_w = Water content in ppm mole
v = Molar volume of water

$\emptyset$ = Fugacity coefficient
R = Universal gas constant
P = Pressure (MPa)
T = Kelvin

The superscript *l* indicates a liquid state, *g* is gas, and *sat* relates to the saturation condition, while the subscript *w* stands for water. Further details of the correlation can be found in their work.

Mohammadi and Richon [13] Correlation

Mohammadi and Richon [13] developed a semi-empirical correlation based on the equality of water fugacity in equilibrium phases for ascertaining the amount of condensable water in a predominantly methane natural gas mixture with hydrates. Equation 2 shows the equation.

$$y_w^H = \frac{p_w^{MT}}{\phi_w^g p} * \exp\left[\frac{v_w^{MT}\left(P - p_w^{MT}\right)}{RT}\right] * \left[\left(1 + C_{small} p\right)^{-v_{small}} + \left(1 + C_{large} p\right)^{-v_{large}}\right] \qquad (2)$$

where:

y_w^H = Water content in equilibrium with hydrates ppm mole,
C = Langmuir constant

The superscript *MT* refers to the metastable state. The subscript small is a small cavity, while large refers to a large cavity. Further details of the correlation can be found in their work.

MATERIALS AND METHOD

The methodology adopted in this study uses the two semi-empirical correlations to ascertain the reliability of a given natural gas–hydrate water content data. To this end, the Mohammadi et al. [12] model for resolving the amount of condensable water of natural gas mixtures without hydrates is depicted as correlation 1. In contrast, the Mohammadi and Richon [13] correlation used for resolving the amount of condensable water of natural gas mixtures with hydrates is depicted as correlation 2.

The percentage absolute average deviation (% AAD) statistical error model estimates the degree of variation between the experimental and predicted water content values. The model is shown in equation 3.

$$\% \, AAD = \frac{1}{n}\left|\frac{W_{Experiment} - W_{Predicted}}{W_{Experiment}}\right| \qquad (3)$$

where:

n = number of data points
W = Water content

A percentage AAD of < 10 is considered a good prediction result. Figure 1 shows the workflow for the study methodology.
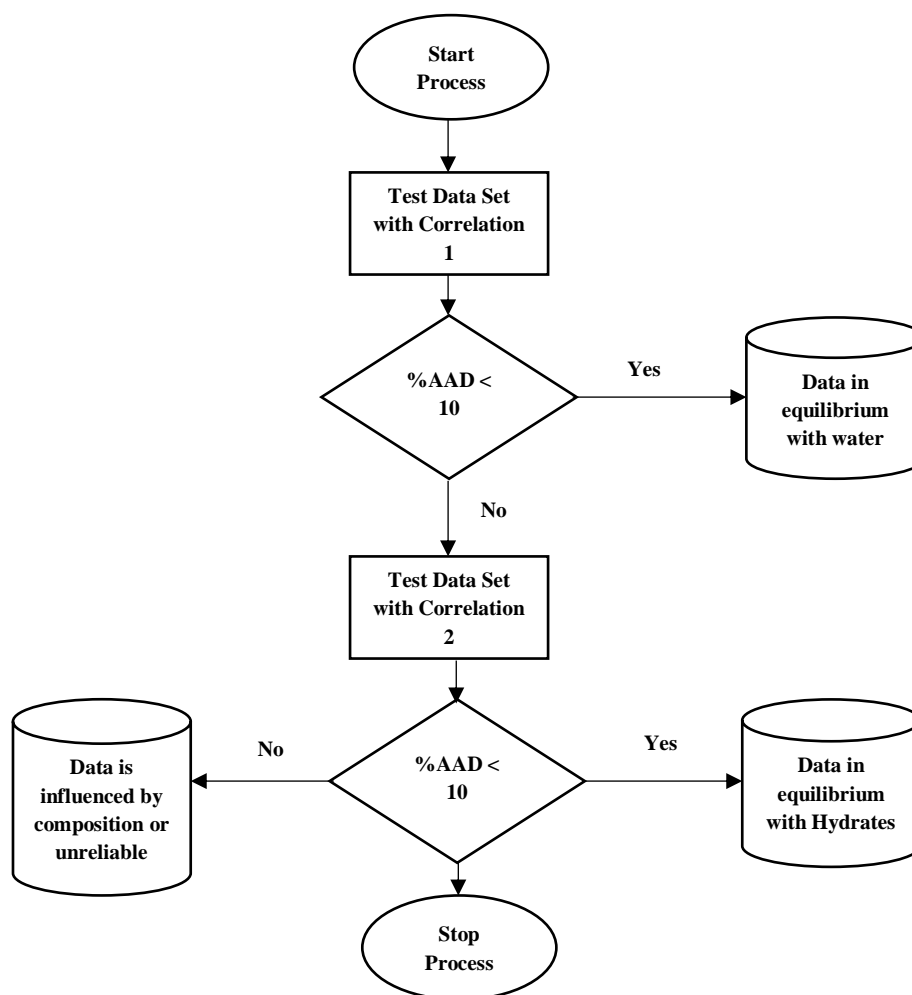
Fig.1 *Workflow for the study methodology.*

For any given water content data set, both correlations 1 and 2 will be tested on the water content data set. If correlation 1 can predict the water content of the data set with a percentage AAD of < 10, then the data set is that of natural gas in equilibrium with liquid water and not hydrates. If not, the data set is tested with correlation 2. If correlation 2 can predict the water content with a percentage AAD of < 10, then the data set is that of natural gas in equilibrium with hydrates. If both correlations 1 and 2 cannot predict the water content with a percentage AAD < 10, then the data set could be in equilibrium with hydrates highly influenced by the gas composition. This is based on the fact that the water content of natural gas in the hydrate region is a strong function of the gas composition [10]. In such instances, more rigorous thermodynamic models should be used for the data validation. If, after validating with the thermodynamic model, the percentage AAD is >> 10, it could imply that the data is unreliable.

The reliability test is conducted on four published data sets of natural gas mixtures with hydrates. The data set used includes:

1. Methane (94.69 mole %) and propane (5.31 mole %) mixture [14].
2. Binary (Methane + Water) mixture [15].
3. Unprocessed natural gas [15].
4. Methane-rich synthetic gas mixture [16]

RESULTS AND DISCUSSION

Table 1 shows the result of the reliability test of the methane and propane mixture data [14]. As seen in the Table, Correlation 1 had a percentage AAD of 26.90, while Correlation 2 predicted the water content with a percentage AAD of 8.19 for the range of pressures and temperatures considered. The large deviation of Correlation 1 from the data set indicates that the gas mixture is not in equilibrium with water. Since Correlation 2 gave an AAD value of less than 10, the water content data is in equilibrium with hydrates. The water content data is reliable and can be used for the stated purpose.

Table 1. Average absolute deviations of correlations for water content of a gas mixture [ppm (mole)] containing methane (94.69 mole %) and propane (5.31 mole %) (Gas gravity = 0.606) in equilibrium with gas hydrates.

Pressure (MPa)	Temperature (K)	Water Content (ppm)		
		Experimental data [14]	Correlation 1	Correlation 2
2.07	234.2	6.86	6.72	7.56
2.07	246.2	24.30	21.40	25.79
2.07	251.7	41.50	34.80	43.53
2.07	260.1	85.20	70.20	92.79
2.07	266.5	162.00	116.00	160.00
2.07	277.2	427.00	252.00	375.90
3.45	234.2	3.47	4.41	4.02
3.45	246.2	13.90	13.90	13.50
3.45	252.1	27.50	23.30	23.46
3.45	263.2	78.80	57.70	62.07
3.45	274.7	188.00	135.00	156.60
6.89	234.2	1.92	2.73	2.12
6.89	246.2	7.03	8.42	7.15
6.89	252.1	12.30	14.00	12.45
6.89	260.0	25.40	26.60	25.15
6.89	263.2	35.80	34.10	33.04
6.89	276.2	104.00	87.20	93.83
10.34	234.2	1.15	2.22	0.96
10.34	246.2	3.75	6.72	3.80
10.34	252.1	7.33	11.11	7.15
10.34	260.1	14.70	21.00	16.05
10.34	266.5	26.80	33.90	29.60
10.34	277.6	81.20	73.30	80.05
		% AAD	**26.90**	**8.19**

Figures 2 to 4 and Table 2 show the results of the validation of the water content data for the binary gas mixture of methane and water in equilibrium with hydrates [15] for pressures of 5 to 15 MPa, and temperatures of 253 to 293 K. Both Correlations 1 and 2 had similar trend with the experimental data. However, Correlation 1 gave a percentage AAD of 8.09, 6.67, and 10.63 for pressures of 5, 10, and 15 MPa, respectively. Correlation 2 had a percentage AAD of 68.21, 69.78, and 92.53 for the same pressure ranges. Interestingly, Correlation 1, for gas–water systems, fit the data set more than Correlation 2, designed for methane-rich gas-hydrate systems. Similarly, Figures 5 and 6 and Table 3 show that the water content data [15] for unprocessed natural gas had a good fit with Correlation 1 with a percentage AAD of 5.57 and 8.48 for pressures of 10 and 15 MPa, respectively, while Correlation 2 had a bad fit with a percentage AAD of 71.75 and 92.33 respectively for the same pressure ranges. Although Correlation 2 is not suited for high-pressure conditions, a bad fit was still obtained even at relatively low pressures. This shows that the water content data [15] for the binary methane + water and unprocessed/raw natural gas is in equilibrium with water and not hydrates.
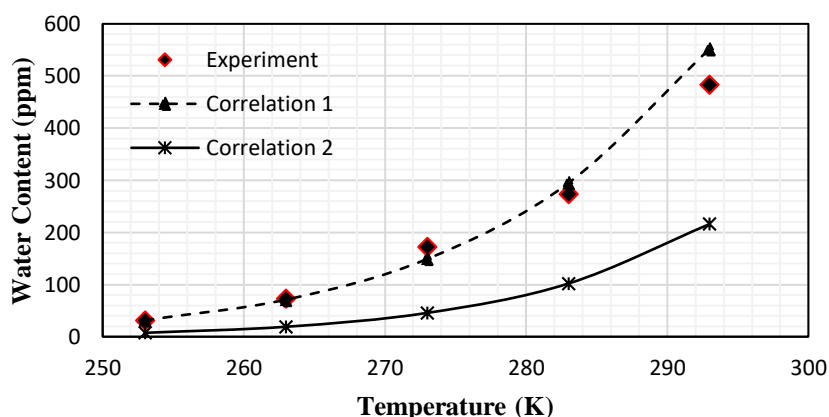

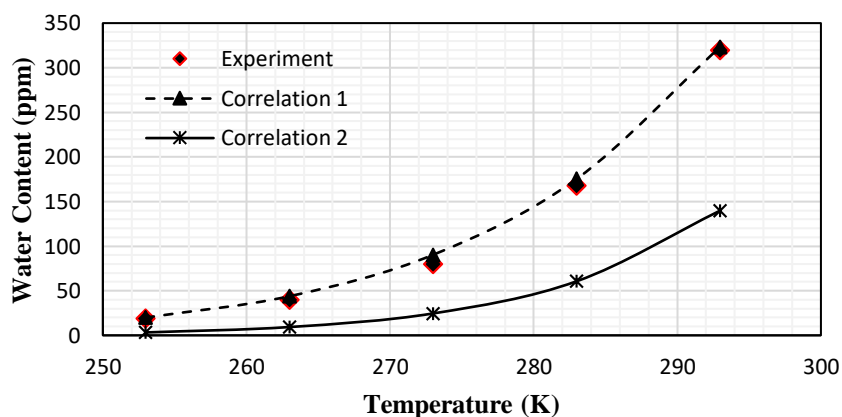*Fig. 2 Water content ppm (mole) for the binary system (water – methane) at 5 MPa*

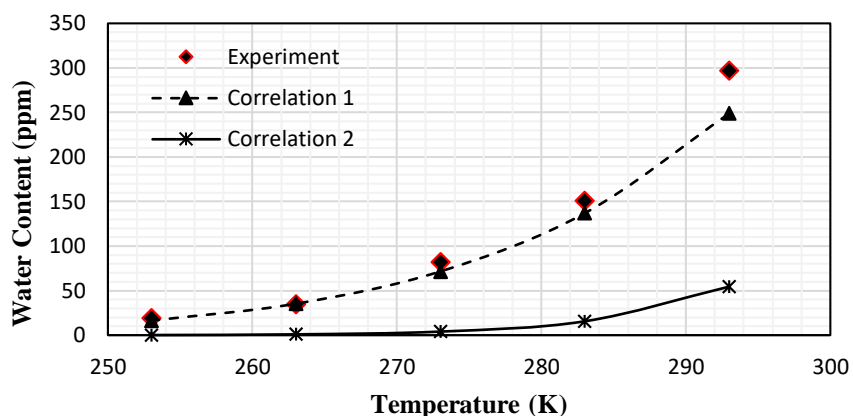*Fig. 3 Water content ppm (mole) for the binary system (water – methane) at 10 MPa*

Fig. 4 *Water content ppm (mole) for the binary system (water – methane) at 15 MPa*

Table 2. *Percentage Average absolute deviations of correlations for binary (methane + water) system*

Pressure (MPa)	Temperature (K)	Water Content (ppm mole)		
		Experiment [15]	**Correlation 1**	**Correlation 2**
5	253	31	31.75	7.84
5	263	73	71.15	19.10
5	273	172	149.20	45.70
5	283	273	294.70	102.00
5	293	483	552.10	216.00
		% AAD	**8.09**	**68.21**
10	253	19	19.97	3.26
10	263	40	43.89	9.33
10	273	80	90.35	24.60
10	283	168	175.50	60.70
10	293	320	323.60	140.00
		% AAD	**6.67**	**69.78**
15	253	19	16.35	0.19
15	263	35	35.31	0.95
15	273	82	71.52	4.06
15	283	151	136.90	15.60
15	293	297	248.90	54.50
		% AAD	**10.63**	**92.53**

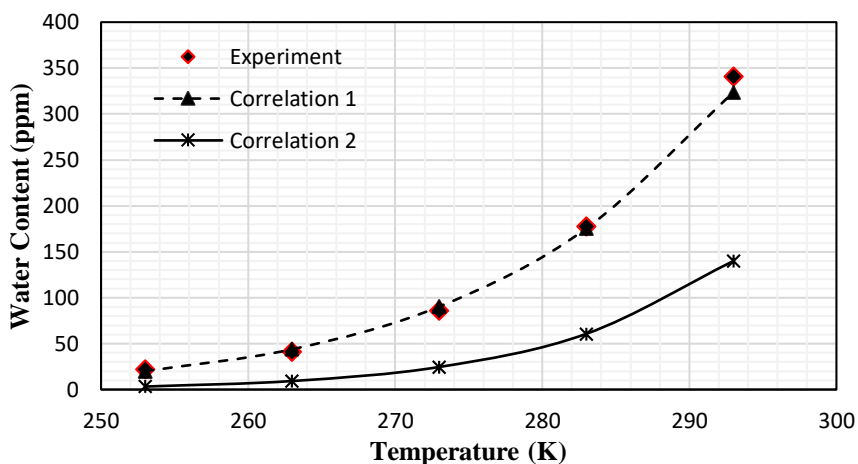***Fig. 5*** *Water content ppm (mole) for unprocessed natural gas at 10 MPa*

Figures 7 to 10 and Table 4 show the results of validating the water content data [16] for synthetic gas mixture in equilibrium with gas hydrates. As seen from the Figures and Table, Correlations 1 and 2 showed bad fits with the data set, with Correlation 2 having the largest deviations of 74.5, 76.9, 73.6, and 72.9 over a temperature range of 253, 263, 273, and 283 K, respectively. The deviation of Correlation 1 confirmed that the synthetic gas mixture is not in equilibrium with water. However, the larger deviation of Correlation 2 could be misleading since the gas composition is considerably different from the mainly methane gas used in developing Correlation 2. Hence, the gas mixture could still be in equilibrium with hydrates but highly influenced by the gas composition. For such cases, a reliable thermodynamic model may be used to validate such data. If a deviation of more than 10 AAD is observed after validation with the thermodynamic model, then the data can be said to be unreliable.
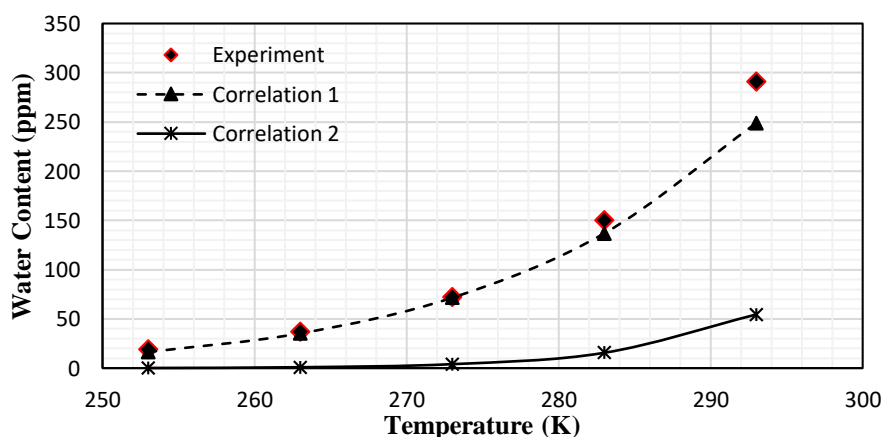

Fig. 6 *Water content ppm (mole) for unprocessed natural gas at 15 MPa*

Table 3. % Average absolute deviations of correlations for unprocessed natural gas system

Pressure (MPa)	Temperature (K)	Water Content (ppm mole)		
		Experiment [15]	Correlation 1	Correlation 2
10	253	22	19.97	3.26
10	263	41	43.89	9.30
10	273	86	90.35	24.60
10	283	178	175.50	60.70
10	293	341	323.60	410.00
		% AAD	**5.57**	**71.75**
15	253	19	16.35	0.19
15	263	37	35.31	0.95
15	273	72	71.52	4.06
15	283	150	136.90	15.60
15	293	291	248.90	54.50
		% AAD	**8.48**	**92.33**

Figures 7 to 10 and Table 4 show the results of validating the water content data [16] for synthetic gas mixture in equilibrium with gas hydrates. As seen from the Figures and Table, Correlations 1 and 2 showed bad fits with the data set, with Correlation 2 having the largest deviations of 74.5, 76.9, 73.6, and 72.9 over a temperature range of 253, 263, 273, and 283 K, respectively. The deviation of Correlation 1 confirmed that the synthetic gas mixture is not in equilibrium with water. However, the larger deviation of Correlation 2 could be misleading since the gas composition is considerably different from the mainly methane gas used in developing Correlation 2. Hence, the gas mixture could still be in equilibrium with hydrates but highly influenced by the gas composition. For such cases, a reliable thermodynamic model may be used to validate such data. If a deviation of more than 10 AAD is observed after validation with the thermodynamic model, then the data can be said to be unreliable.
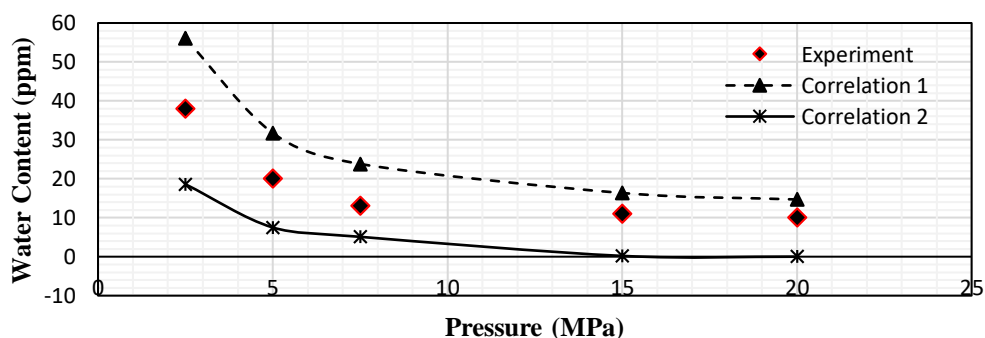

Fig. 7 Water content (ppm mole) for synthetic natural gas mixture at -20°C ±0.1

Table 4. Percentage average absolute deviations of correlations for synthetic natural gas system

Pressure (MPa)	Temperature (K)	Water Content (ppm mole ±5 ppm mole or 4%, whichever is the greater)		
		Experiment [16]	Correlation 1	Correlation 2
2.50	253	38	56.08	18.60
5.00	253	20	31.75	7.50
7.50	253	13	23.81	5.10
15.00	253	11	16.35	0.19
20.00	253	10	14.69	0.00
		% AAD	**57.00**	**74.50**
2.50	263	99	127.10	48.30
5.00	263	56	71.15	19.10
7.50	263	46	52.84	13.30
15.00	263	26	35.31	0.95
20.00	263	26	31.26	0.00
		% AAD	**25.26**	**76.90**
2.50	273	233	269.00	117.00
5.00	273	121	149.20	45.70
7.50	273	87	109.70	32.30
15.00	273	60	71.52	4.10
20.00	273	55	62.44	0.01
		% AAD	**19.52**	**73.61**
2.50	283	543	536.40	265.00
5.00	283	279	294.70	102.00
7.50	283	198	214.90	73.60
15.00	283	122	136.90	15.60
20.00	283	106	117.90	0.14
		% AAD	**7.76**	**72.91**

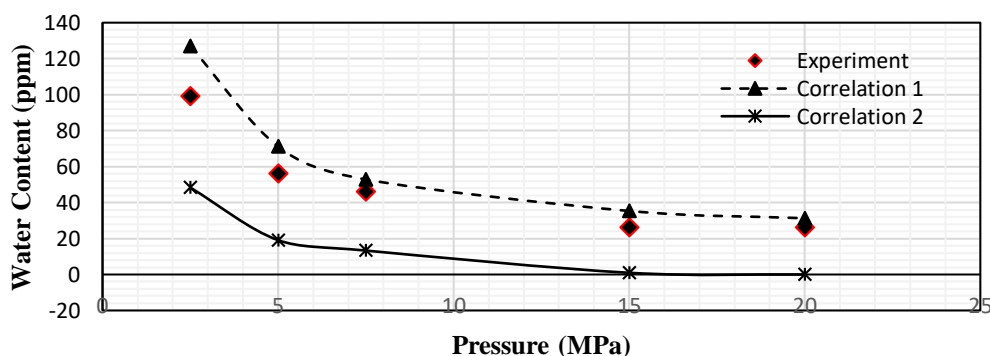*Fig. 8 Water content (ppm mole) for synthetic natural gas mixture at -10°C ±0.1*

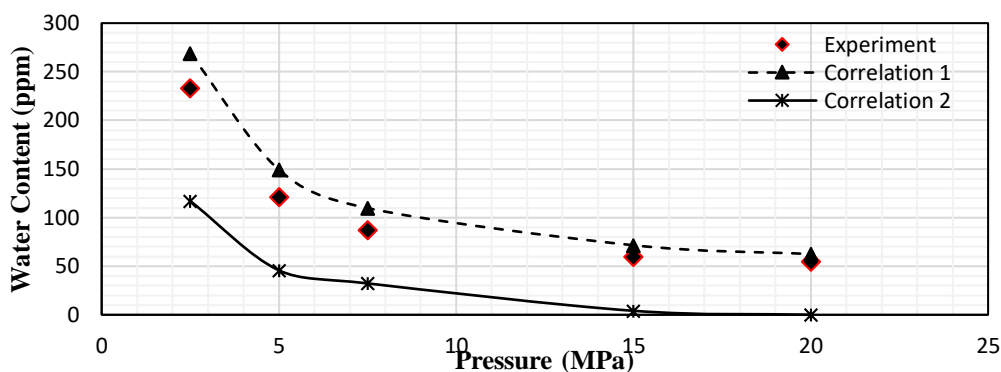**Fig 9.** *Water content (ppm mole) for synthetic natural gas mixture at   0°C ±0.1*

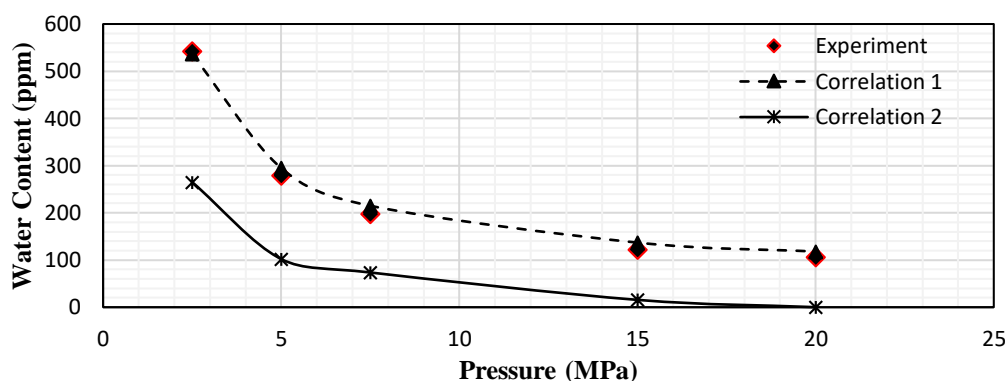**Fig 10.** *Water content (ppm mole) for synthetic natural gas mixture at   10°C ±0.1*

CONCLUSION

The reliability of the water content data for natural gas-hydrate systems is imperative for the effective design of dehydration facilities and the prevention of flow assurance problems. Due to the difficulty in accurately measuring the water content of these systems at low temperatures, some of the existing published water content data have been entirely erroneous and unreliable. This study has presented a methodology for determining the reliability of published water content data for natural gas in equilibrium with hydrates, using two established simple-to-use semi-empirical correlations.

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