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Improving pH Prediction for High Pressure and High Temperature Applications in Oil and Gas Production

C. Plennevaux
T. Cassagne
M. Bonis
TOTAL
Avenue Larribau, Pau Cedex 64018
France

J. Kittel
F. Ropital
IFP Énergies nouvelles
Rond-point de l'échangeur de Solaize BP3 69360
Solaize
France

N. Ferrando
IFP Énergies nouvelles
1-4 avenue de Bois-Préau, 92852 Rueil-
Malmaison
France

M. Frégonèse
B. Normand
MATEIS, INSA de Lyon
CNRS UMR 5510 Avenue Jean Capelle
Villeurbanne Cedex 69621
France

Abstract

pH prediction represents a crucial step before selecting materials for use in sour oil and gas wells as regards weight loss corrosion and H₂S cracking. Among the numerous parameters which determine the equilibrium pH, important ones are CO₂ and H₂S partial pressures (P_{CO_2} and P_{H_2S} respectively), the total pressure, the ionic strength and the chemical composition of the solution, and the temperature. Most models used by oil and gas operators present a too narrow range of validity for these parameters, which makes them inappropriate for high pressure and high temperature (HPHT) fields or for CO₂ reinjection. This paper presents modeling improvements which allows extending the prediction validity in temperature and pressure to respectively 200 °C and 1,000 bar of total pressure, and for an ionic strength up to 5 mol.kg⁻¹.

These improvements take into account the fugacities in gas phase of CO₂ and H₂S as determined by the Soreide and Whitson formalism. The influence of water and CH₄ pressure is also taken into account up to several hundred bars. Activity coefficients in the water phase are calculated using the Pitzer model. The consistency of the model is verified by comparison with experimental measurements of pH under high pressure.

It is then applied to oil and gas applications at high pressure and high temperature. The impact of the new calculation method is discussed both for pH evaluation and also for H₂S activity, with strong implications for the evaluation of SSC risks.

Keywords: pH, CO₂, H₂S, high pressure, high temperature

Introduction

Produced waters contain dissolved acid gases such as carbon dioxide (CO₂) and sometimes hydrogen sulfide (H₂S). These dissolved gases induce uniform corrosion of low alloy steels. Risks of hydrogen embrittlement and cracking are also specifically associated with wet H₂S. The risk level is strongly related to in-situ pH.¹⁻⁵

To make the most accurate material selection in regard to the application, industrial companies and research institutes have developed prediction models of CO₂ and H₂S corrosion. They provide pH evaluation from water composition and in situ temperature and partial pressures of acid gases. However most of the usual models are limited to low pressures, relatively low temperatures and to slightly concentrated brines solutions. This is the case of the model of some of the authors' company, which is limited to 20 bar of acid gas and 150 °C. These limitations were not a problem for typical oil and gas fields operated from the eighties to 2,000. However, the increasing number of high pressure (HP) and high temperature (HT) oil and gas fields being developed requires these pH calculation tools to be extended to higher limits of use. The goal of this work is therefore to extend the existing pH evaluation model to HPHT applications and to highly concentrated brines.

Modeling approach

Detailed description of the model was given elsewhere.⁶ We only present in this section the approach of the main improvements of the new model, compared to the previous one used by the author's company.

The evolution of the model comprises two major steps: a better description of gas solubilities, taking into account the fugacity of gaseous components ; an improvement of chemical equilibria description through the calculation of activity coefficients of species in the liquid phase.

The main differences between the old model and the new model are presented below.

Calculation of Gas Solubility

The easiest method for gas solubility calculation uses a simplified expression of the Henry's law, with the assumption of ideal gas and liquid phases. Then, at a given temperature, the concentration of dissolved component *i* (*c_i*) is directly proportional to its partial pressure (*P_i*):

$$H_i(T) = \frac{P_i}{c_i} \quad (1)$$

Where:

H_i is the Henry constant for species *i*, and depends only on temperature.

However, the assumption of ideal gas and liquid phases is extremely restrictive, and cannot reasonably be applied in most conditions encountered in oil and gas production. Therefore, it was proposed by several authors to use apparent solubility constants (*S_{app,i}*), depending not only of temperature, but also of pressure (*P*) and of the ionic strength (*IS*). Then, it is still possible to relate the mole concentration of dissolved gas and partial pressures, with the same kind of expression:

$$S_{app,i}(T, P, IS) = \frac{c_i}{P_i} \quad (2)$$

The consistency of this method deeply depends on the evaluation of the apparent solubility constant. Several expressions obtained by numerical adjustments on experimental data have been proposed for CO₂ and H₂S, as described in Table 1. This method is currently employed in most models used by oil and gas operators, and especially by the model of some of the author's company. However, most of these expressions have a narrow validity domain with temperature, pressure and ionic strength, even if this range was sufficient at the time when they were established.

Table 1
Empirical expressions used for solubility calculations of CO₂ or H₂S

Constant	Expression
S_{CO_2}	$-\log(S_{CO_2}) = -\log\left(\frac{14.5}{1.00258}\right) + 2.27 + 5.65 \times 10^{-3} \times T_f - 8.06 \times 10^{-6} \times T_f^2 + 0.075 \times IS^7$ $-\log(S_{CO_2}) = -\frac{2385.73}{T_K} + 14.018 - 0.015T_K + (0.286 - 6.167 \cdot 10^{-4} T_K) IS^8$ $S_{CO_2} = 55.5084 \cdot e^{-\left(4.8 + \frac{3934.4}{T_K} - \frac{941290.2}{T_K^2}\right)} \cdot 10^{-(1.790 \cdot 10^{-4} P + 0.107 IS)} (0^\circ\text{C} - 80^\circ\text{C})^9$ $S_{CO_2} = 55.5084 \cdot e^{-\left(\frac{1713.53 \left(1 - \frac{T_K}{647}\right)^{1/3}}{T_K} + 3.875 + \frac{3680.09}{T_K} - \frac{1198506.1}{T_K^2}\right)} \cdot 10^{-(1.790 \cdot 10^{-4} P + 0.107 IS)} (80^\circ\text{C} - 200^\circ\text{C})$
S_{H_2S}	$S_{H_2S} = e^{-41.0563 + 66.4005 \left(\frac{100}{T_K}\right) + 15.1060 \ln\left(\frac{T_K}{100}\right)} 10$ $S_{H_2S} = 10^{\frac{-3898.56}{T_K} - 12.4914 \ln T_K + 0.00831109 T_K + 82.7622} 11$ $S_{H_2S} = \frac{10}{e^{-3.3747 + 0.072437 T_K - 1.10765 \cdot 10^{-4} T_K^2 - \frac{1549.159}{T_K} + 0.144237 \ln T_K}} 12$ $S_{H_2S} = 10^{\left(634.27 + 0.2709 T_K - 0.11132 \cdot 10^{-3} T_K^2 - \frac{16719}{T_K} - 261.9 \log T_K\right)} 13$ $S_{H_2S} = 10^{-0.71742672 - 0.012145427 T_c + 5.6659982 \cdot 10^{-5} T_c^2 - 8.1902716 \cdot 10^{-8} T_c^3} 14, 15$

T_f , T_c and T_k represent temperature in Fahrenheit, Celsius, or Kelvin.

In order to increase the prediction ability to HPHT conditions, it is necessary to use the ensemble Henry's law,¹⁶⁻¹⁸ which takes into account gaseous components fugacity and their activity in the liquid phase. The rigorous expression is the following:

$$H_i(T) = \frac{\Phi_i \cdot P_i}{\gamma_i \cdot c_i \cdot \exp\left[\int (v_i^\infty / RT) \cdot dP\right]} \quad (3)$$

Where:

c_i is the concentration of the component i in the liquid phase

$H_i(T)$ is the Henry's constant characterizing the solubility of the gas in water

P_i is the partial pressure of component i

The activity coefficient γ_i accounts for non-ideality of dissolved gas, the exponential term is known as the Poynting correction considering the effect of high pressures on the partial molar volume of the solute under infinite dilution and the fugacity coefficient Φ_i corrects the gas phase for non ideal behavior.

This approach is used in our work. The Henry's constants $H_i(T)$ are calculated using Dhima's correlations.¹⁹ Correlations allowing to describe equilibrium constants $K(T)$ on a wide range of temperature are selected in the literature.²⁰⁻²⁴ Fugacity coefficients in the gas phase are calculated using the Soreide and Whitson's model²⁵ and activity coefficients in the liquid phase are calculated applying Pitzer's model.²⁶

In order to make the model modification as simple as possible, we simply replaced the old expressions of apparent solubility constants (2) by new expressions derived from (3):

$$S_{app,new,i} = \frac{\Phi_i}{H_i(T) \cdot \gamma_i \cdot \exp\left[\int (v_i^\infty / RT) \cdot dP\right]} = \frac{c_i}{P_i} \quad (4)$$

Description of Chemical Equilibria in the Liquid Phase

The approach used for chemical reactions in the solution is extremely similar.

The usual approach in most models used by oil and gas companies considers apparent constants to describe chemical equilibria.

As an illustration, different expressions that are used to describe the equilibrium constant of the first dissociation of CO₂ (K_1) or H₂S (K_1') are presented in Table 2.

Table 2
Examples of empirical expressions used for chemical equilibrium constants.

Constant	Expression
K_1	$-\log(K_1) = 3.82 - 1.594 \times 10^{-3} \times T_f + 8.52 \times 10^{-6} \times T_f^2$ $-3.07 \times 10^{-5} \times p - 0.4772 \times I^{0.5} + 0.118 \times I$
K_1'	$-\log(K_1') = 10.61 - 4.97 \times 10^{-3} \times T_f + 1.331 \times 10^{-5} \times T_f^2$ $-2.624 \times 10^{-5} \times p - 1.166 \times I^{0.5} + 0.3466 \times I$

By using these expressions, one is able to determine the relative concentrations of the species involved in the reactions:

$$K_1(T, IS) = \frac{c_{HCO_3^-} \times c_{H^+}}{c_{CO_2}} \quad (5)$$

$$K_1'(T, IS) = \frac{c_{HS^-} \times c_{H^+}}{c_{H_2S(d)}} \quad (6)$$

As in the case of gas solubilities, this approach using empirical expressions for the apparent chemical equilibrium constants is only valid in a narrow range of temperature, pressure and ionic strength.

In order to extend the validity domain, we replaced these empirical expressions by new expressions including activity coefficients derived from Pitzer's model.²⁷

Similarly to solubility constants, new expressions of chemical equilibrium constant can be derived from the rigorous expression as:

Rigorous expression:

$$K(T) = \prod_i (\gamma_i \cdot c_i)^{v_i} \quad (7)$$

New expression of apparent constants:

$$K_{app,new} = K(T) \times \prod_i (\gamma_i)^{-v_i} = \prod_i (c_i)^{v_i} \quad (8)$$

In these expressions, $K(T)$ is the equilibrium constant of the chemical reaction, γ_i , c_i and v_i are respectively the activity coefficient, the concentration and the stoichiometric coefficient of component i , corresponding either

to a reactant or to a product. $K_{app,new}$ represents the new expression that was implemented in the model to replace the old empirical expressions as those of Table 2.

Finally, the calculation method of pH is classically derived from the electroneutrality equation as described elsewhere.²⁸ Once H^+ concentration is determined, pH is calculated from H^+ activity according to:

$$pH = -\log a_{H^+} = -\log(\gamma_{H^+} \cdot c_{H^+}) \quad (9)$$

In this expression, a_{H^+} is the activity, γ_{H^+} is the activity coefficient and c_{H^+} is the concentration of H^+ in the produced water.

Validity Domain, Capabilities, and Limitations of The New Model

At the present time, the improvements brought by the new model only apply to CO_2 , H_2S , CH_4 and H_2O for the gas phase. In the liquid phase, ionic species that are considered for calculations of activity coefficients are Ca^{2+} , Na^+ , Cl^- , H^+ , HCO_3^- , CO_3^{2-} , HS^- , S^{2-} and HO^- .

The main input parameters of the model are: the total pressure and the partial pressures of CO_2 , H_2S and CH_4 , the temperature and the ionic composition of the solution (Ca^{2+} , Na^+ , Cl^- , HCO_3^-).

The main output data are: in-situ pH, gases fugacities, concentration and activities of all dissolved species.

Precipitation of solids is not considered. Acetate is also not included in this first version of the new model, since interaction terms for the Pitzer model²⁷ for acetate species are hardly documented in the literature.

As a first approximation, the validity domain can be estimated from the validity of individual elements used in the new model. The main limitations arise from the validity domains of equilibrium constants and of interaction parameters, and we can thus expect good predictions up to 200 °C, 1,000 bar of total pressure, and ionic strengths up to 5 mol.L⁻¹.

A discussion of the validity domain based on comparisons with experimental data and other models is given in the next section of this paper.

COMPARISON WITH EXISTING DATA AND OTHER MODELS

Only a few published papers were found with pH measurements at high pressure, high temperatures and high salinities. None of them covered at the same time the expected validity domain of our new model, i.e., a high temperature, a high pressure and a high ionic strength. Thus, analysis of the new model capabilities could only be performed for one or two parameters at a time.

A selection of comparisons between the new model and data from the literature is provided from Figure 1 to Figure 5. For the sake of comparison, predictions calculated with the old model are also provided. We used two different methods for these calculations with the old model: i/ a strict application using partial pressures of CO_2 and H_2S as inputs (it is reminded that extrapolation above the validity domain shall be avoided); ii/ modified method using fugacity of CO_2 and H_2S as input (referred by fugacity-corrected in the following). In the latter case, fugacity coefficients were calculated by the Soreide and Whitson's model. It is important to note however that the old model should not be applied above 120 °C, 20 bar of CO_2 and for an ionic strength exceeding 0.75 mol/L.

Figure 1 presents H_2S solubility data obtained by Ng et al.²⁹ Experiments were conducted at 49 °C in pure water. The total gas pressure was varied from a few bar to 700 bar, with a constant ratio $CH_4/C_3H_8/H_2S/CO_2$ (71/4/19/6).

Calculated data were obtained with the old model, using only the CO_2 and H_2S partial pressure, or after the fugacity correction. Calculations with the new model assumed that the hydrocarbon was 100% CH_4 instead of 95/5 CH_4/C_3H_8 .

The best results are obtained with the new model, with good agreement with the experimental data up to 700 bar of total pressure, corresponding to 133 bar H₂S and 42 bar CO₂. However, applying fugacity correction with the old model significantly increases the pressure validity domain. For the specific conditions of this example, the old model overestimates the new model prediction of more than 10% above 30 bar of total pressure, while fugacity correction allows to maintain less than 10% error up to 180 bar.

Figure 2 and Figure 3 compare CO₂ solubility data obtained by Rumpf et al.³⁰ and by Duan and Sun³¹ in concentrated NaCl solution up to 200 °C and 1,500 bar CO₂.

The new model presents a good agreement with the experimental data up to 1,500 bar CO₂, whereas the old model presents significant error at high pressure CO₂, even after fugacity corrections. The predictions of our model are extremely close to those obtained with the model of Duan and Sun.

Figure 4 shows pH values in pure water under CO₂ pressure up to 350 bar. Experimental data was obtained by Meysami et al. in autoclave.³² The new model reproduce the pH evolution with a good accuracy in all P_{CO2} domain. For comparison, calculations were also performed with the old model after fugacity correction, and with the Norsok model. They both give acceptable pH values up to 50 to 100 bar CO₂.

Figure 5 illustrates the impact of the ionic strength on pH. Experimental data was obtained at 25 °C and 1 bar CO₂ by Hinds et al.³³ In the same paper, these author's compared the prediction of two models of oil and gas companies. The results are reproduced for comparison with our old and new models. The new model gives similar results than the two models reported. The old model tends to underestimate the pH value for NaCl concentration below 1 mol/L.

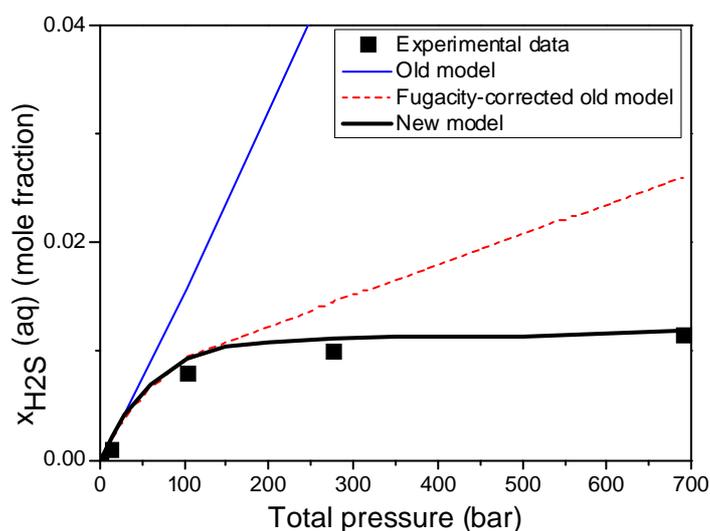


Figure 1: Predictions of H₂S solubility in pure water under pressure of 75% CH₄-C₃H₈ (95:5 mole ratio) and 18% H₂S and 6% CO₂ at 49 °C. Comparisons with experimental data from Ng et al.

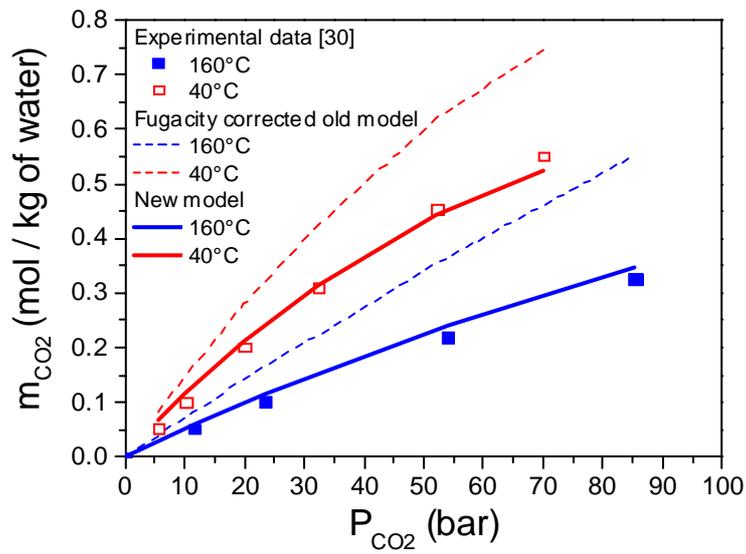


Figure 2: Predictions of CO₂ solubility in 4 mol/kg NaCl water at different temperatures. Comparisons with experimental data from Rumpf et al.

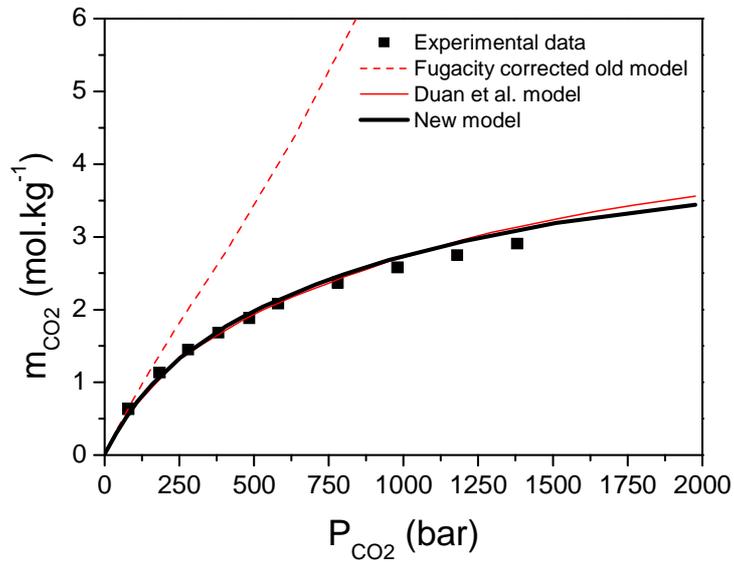


Figure 3: Evolution of CO₂ solubility in 1 M NaCl solution at 200 °C. Comparison with experimental data³⁴ and with another model.

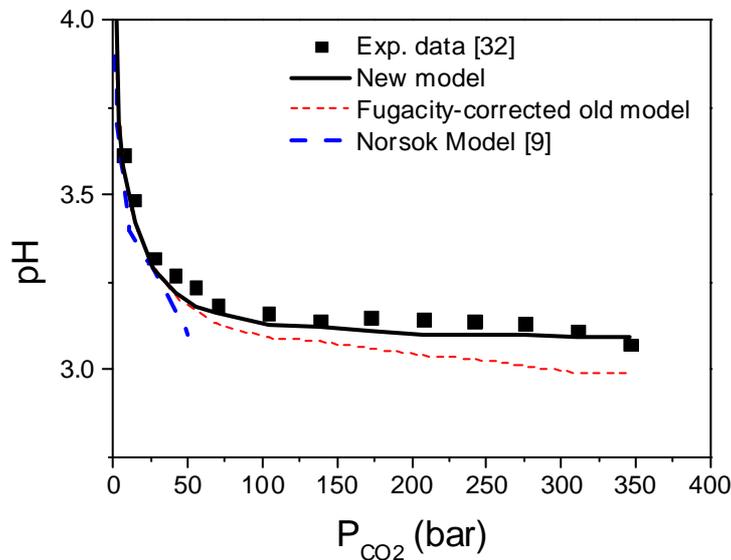


Figure 4: Evolution of the pH value in pure water with CO₂ partial pressure at 42 °C. Comparisons with experimental data obtained by Meyssami et al. and with predictions calculated with the Norsok model.

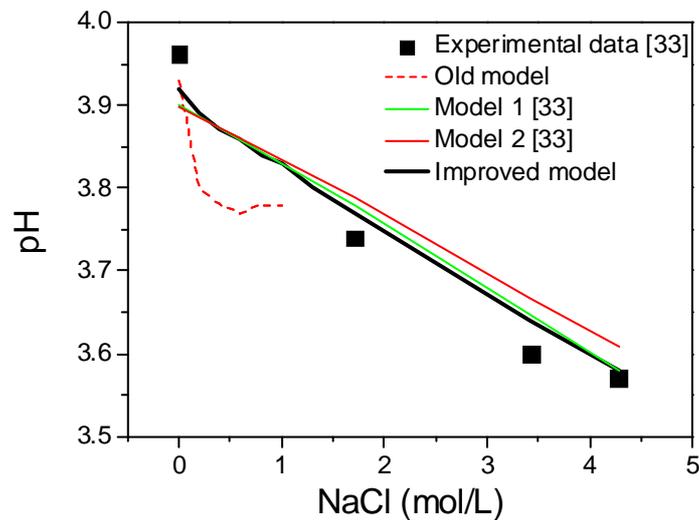


Figure 5: Evolution of in-situ pH at 25 °C and 1 bar CO₂ in water with various amount of NaCl. Comparison with experimental data and with other models given.

A synthetic view of the range of evolution for the main parameters is provided in Table 3. Although there exists no set of experimental data that was obtained at high pressure, high temperature and high ionic strength in the same experiment, the validity domain of the theoretical models used versus individual parameter has been verified up to 200 °C, 4.5 mol/L NaCl and 2,000 bar total pressure.

It appears also quite clearly that applying fugacity correction with the old model is not sufficient to accurately predict CO₂ and H₂S solubilities. Similar evidence was already given by Nelson et al. On the other hand, it also appears that several models already exist giving accurate prediction of pH and solubilities. Most of these models use rigorous thermodynamic laws. Such models have to be used for the evaluation of HP/HT environments.

Table 3:
Range of tested parameters in Figure 1 to Figure 5.

T (°C)	ionic strength (mol/L)	P _{CO2} (bar)	P _{H2S} (bar)	total pressure (bar)	pH	Figure
49	0	0 – 42	0 – 133	0 – 700	no	1
40 – 160	4	5 – 90	no	5 – 90	no	2
200	1	0 – 2000	no	0 – 2000	no	3
42	0	0 – 350	no	0 – 350	yes	4
25	0 – 4.5	1	no	1	yes	5

APPLICATION TO PRACTICAL SITUATIONS

In order to illustrate the importance of using advanced thermodynamic models, two case studies simulating wellbore environment are presented.

Case Study 1

For this first case study, we considered a constant acid gas content consisting of 50 bar CO₂ and 0.1 bar H₂S. Methane pressure is taken as a parameter and varies from 50 to 1,000 bar. Water composition is also variable. The worst situation consists in condensed water. Intermediate situations consisting in formation water at different levels of dilution in condensed water were also examined. The following composition of formation water was used: Na⁺ = 63 g/L (2,750 mM); Ca²⁺ = 20 g/L (500 mM); Cl⁻ = 131 g/L (3,700 mM); HCO₃⁻ = 3 g/L (50 mM).

As shown in Figure 6, increasing the total pressure induces an important increase of in situ pH at constant acid gas partial pressure. The effect is mainly due to the decrease of acid gas fugacity when the total pressure increases. However, fugacity correction is not sufficient at the highest pressure: while fugacity reaches a plateau, pH continues to increase, because of the decrease of H⁺ activity coefficient.

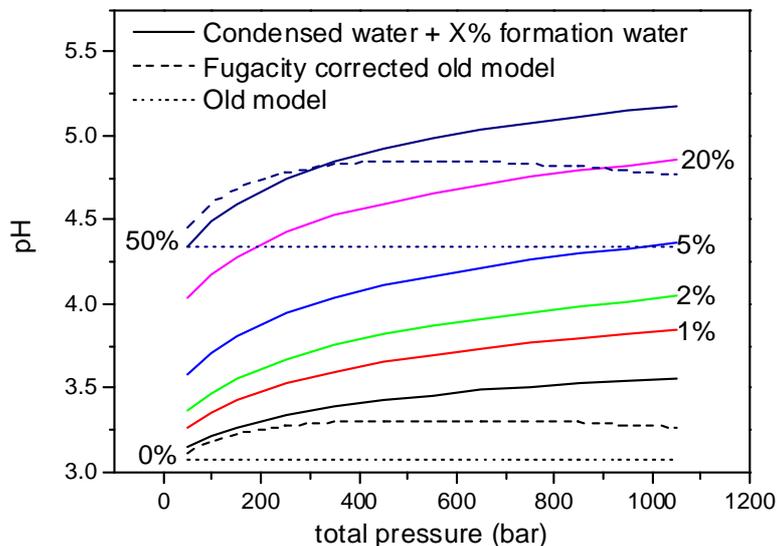


Figure 6: Evolution of in-situ pH with CH₄ pressure in condensed water and in formation water at variable dilution ratios, at 21 °C, 50 bar CO₂ and 0.1 bar H₂S. Comparisons between new model and old model with or without fugacity correction.

For the same parametric matrix, we also calculated H₂S fugacity. The results are shown in Figure 7. As expected, fugacity decreases strongly when the total pressure increases. H₂S fugacity correction could be applied for fit-for-purpose (FFP) testing. In the 50% formation water of this example at 1,000 bar CH₄, 50 bar CO₂ and 0.1 bar H₂S, applying the old pH model without fugacity correction suggests testing at pH value of 4.3 and 0.1 bar H₂S. On the contrary, with the new model and H₂S fugacity, FFP tests could be performed at pH value 5.2 and 0.02 bar H₂S, though the latter presents less conservatism for materials selection.

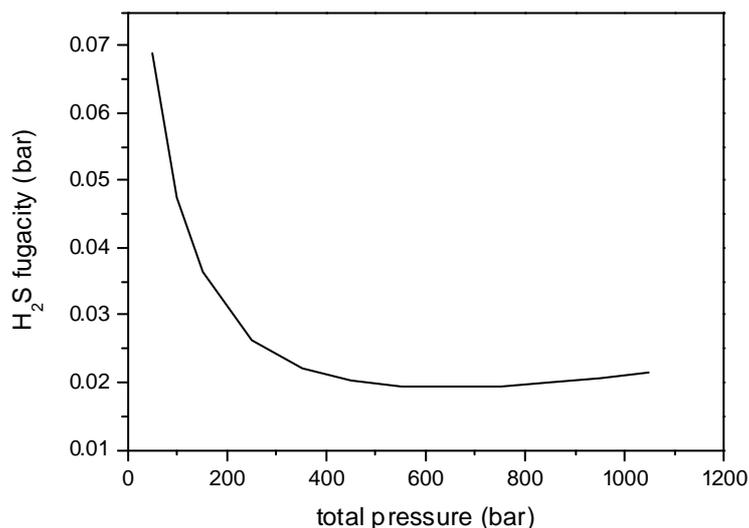


Figure 7: Evolution of H₂S fugacity with CH₄ pressure at 21 °C, 50 bar CO₂ and 0.1 bar H₂S.

Case Study 2

For the second case study, the gas composition was maintained constant, i.e. 90% CH₄, 10 % CO₂ and 200 ppmv H₂S. Only the total pressure varied from 50 bar to 1000 bar. The water composition was also constant, and contained 17 g/L Na⁺ (750 mM), 27 g/L Cl⁻ (750 mM), 0.12 g/L Ca²⁺ (3 mM) and 0.37 g/L HCO₃⁻ (6 mM). Calculations were made at 21 °C and 120 °C. Water composition and temperature range were chosen to fit in the validity domain of the old model used as reference for this paper. pH calculations were also made with the Norsok model for comparison.

pH evolution is shown in Figure 8. The new model always predicts higher pH than the other models. The lower pH values are obtained with the old model, while Norsok model and fugacity corrected old model give intermediate pH values. If the new model is thought to be more accurate, other predictions are more conservative.

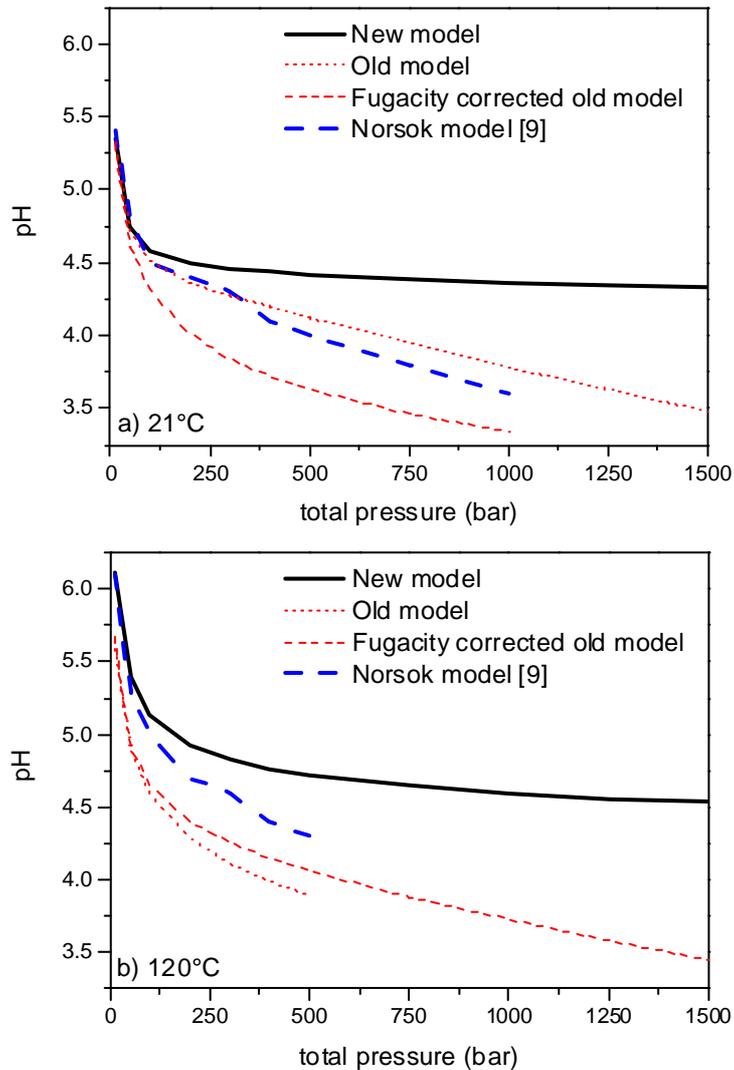


Figure 8: Evolution of in-situ pH with total pressure of CH₄ (90%), CO₂ (10%) and H₂S (0.02%) in simulated formation water at 21 °C (a) and 120 °C (b). Comparisons between the new model, the old model with or without fugacity corrections, and the Norsok model.

Comparison of FFP test conditions predicted with the different models was also undertaken. The results are plotted in the SSC severity diagram in Figure 9. Important differences are observed at high pressure. For instance, at 21 °C and with a total pressure of 1,000 bar (with 10% CO₂ and 0.02% H₂S), the new model predicts a pH value of 4.36 and H₂S fugacity of 0.04 bar. This condition lies in region 2 of the SSC severity diagram. For the same field conditions, using the old model with or without fugacity correction moves to SSC region 3, with respectively a pH value of 3.78 and H₂S fugacity of 0.04 bar, or a pH value of 3.34 and H₂S partial pressure of 0.2 bar.

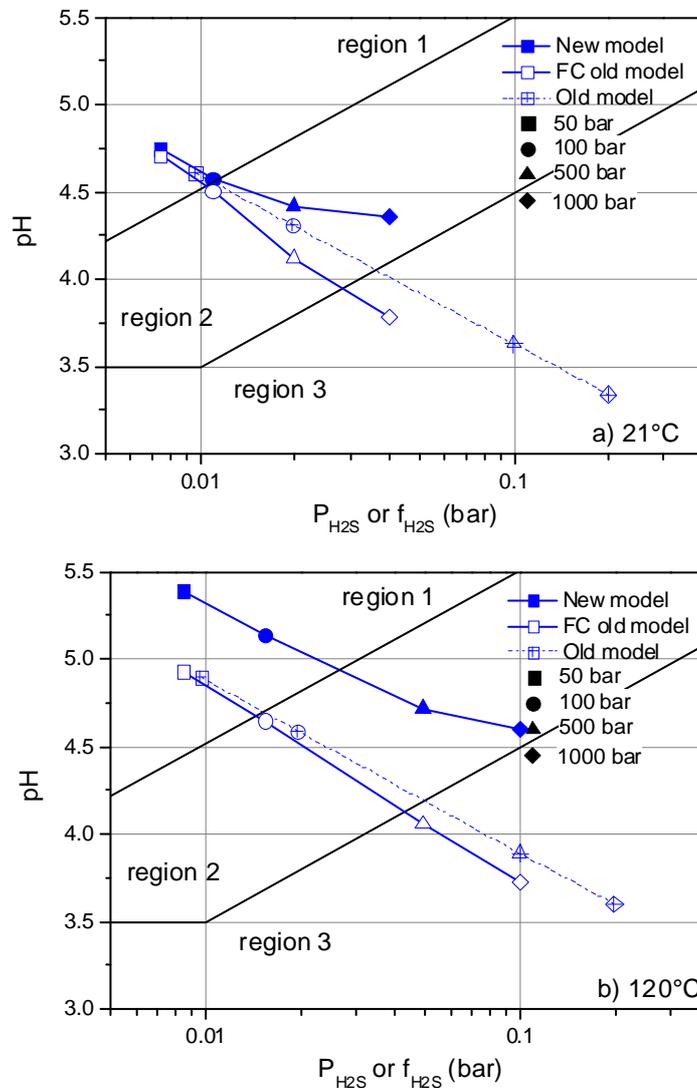


Figure 9: Comparisons of FFP test conditions in the SSC severity diagram for the examples of Figure 8. Comparisons between the new model and the old model with or without fugacity correction.

CONCLUSION

The in-situ pH is one of the most important parameters for material selection in the oil and gas production. Accurate pH prediction is therefore required. Lots of predictions tools were designed in the 80's and were adapted to temperatures lower than 150 °C, maximum pressures of 50 bar and slightly concentrated solutions (up to 1 mol/L). Since modern thermodynamic models were not available at that time, these calculation tools had to consider ideal gases and solutions, compensated by the use of apparent constants obtained by numerical adjustments on experimental data. However, the increasing interest of HPHT fields and of gas fields with high CO₂ contents requires models with extended validity domain. Using old models with fugacity correction of acid gas partial pressure allows to extend the validity domain to intermediate pressure. However, good predictions in HPHT conditions require using more recent thermodynamic models, to assess gases fugacity and activity coefficients of chemical species in the liquid phase.

Extension of the validity domain of the old model used by some of the authors was described. It uses fugacity coefficients calculated with Soreide and Whitson's model. The effect of high concentrations of salts on the activity of chemical species in the liquid phase is modeled using Pitzer's formalism.

Using such models allows more accurate pH and H₂S fugacity predictions, with potential impacts on FFP testing. New calculations are usually less conservative than the former ones, with higher pH values and lower H₂S activity.

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