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# pH prediction in concentrated aqueous solutions under high pressure of acid gases and high temperature

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## Abstract

pH prediction represents a crucial step before selecting materials for use in sour oil and gas wells as regards weight loss corrosion and H<sub>2</sub>S cracking. Among the numerous parameters which determine the equilibrium pH, important ones are CO<sub>2</sub> and H<sub>2</sub>S 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 CO<sub>2</sub> reinjection. This paper presents modeling improvements which allows extending the prediction validity in temperature and pressure to respectively 200-250°C and above 200 bar of acid gases, and for an ionic strength up to 5 mol.kg<sup>-1</sup>.

The new model takes into account the fugacities in gas phase of CO<sub>2</sub> and H<sub>2</sub>S as determined by the Soreide and Whitson formalism. The influence of water and CH<sub>4</sub> pressure is also taken into account up to several hundred bars. Activity coefficients in the water phase are calculated using the Pitzer model. The model is verified by comparison with experimental measurements of pH under high pressure.

# 1 Introduction

Produced waters contain dissolved acid gases such as carbon dioxide (CO<sub>2</sub>) and sometimes hydrogen sulfide (H<sub>2</sub>S). These dissolved gases induce uniform corrosion of low alloy steels. Risks of hydrogen embrittlement and cracking are also specifically associated with wet H<sub>2</sub>S. 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 CO<sub>2</sub> and H<sub>2</sub>S corrosion. They provide pH evaluation from water composition and in-situ temperature and partial pressures of acid gases. However usual models are limited to low pressures, relatively low temperatures and to slightly concentrated brines solutions. This is the case of the company model of some of the authors, 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 2000. 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.

## 2 Background

Before presenting the new model in detail, a brief description of actual methods of pH calculation in oil and gas environments is proposed. Two groups of reactions are usually considered: i/ dissolution of acid gases in the solution and ii/ chemical dissociation of weak acid components.

The corresponding reactions are described below.

At the liquid/gas interface, a quantity of CO<sub>2</sub> and H<sub>2</sub>S dissolves in the aqueous solution according to reactions (a) and (b) :



In the liquid phase, dissolved carbon dioxide hydrates to carbonic acid following reaction (c).



Carbonic acid and hydrogen sulfide are weak diacids. They are likely to dissociate according to reactions (d) to (g).



The dissolution of acid gases is described by solubility constants  $S_{CO_2}$  and  $S_{H_2S}$  and equilibrium constants  $K_{hyd}$ ,  $K$ ,  $K'_1$ ,  $K_2$  and  $K'_2$  define chemical equilibria in the liquid phase as the ratios between the products and the reactants. Theoretically, solubility constants and equilibrium constants depend only on temperature as long as fugacities are used. However for simplicity these constants are frequently

expressed vs concentrations and partial pressures. Consequently these constants must include the effects of pressure and ionic strength. Empirical expressions versus temperature and / or ionic strength are often used to describe these equilibrium constants, the effect of pressure being frequently not included. Some of them can be found in references [6-9].

The main advantage of such methodology is that it allows using the simple formalism of partial pressures and concentrations in a range of temperature, pressure and ionic strength. However, the validity domain remains limited to low pressures, low temperatures and to slightly concentrated brines solutions. As reported in the literature [10] most of industrial models, including the model of some of the authors' company, are limited to 150°C, 20 bar of CO<sub>2</sub> and an ionic strength of 1 mol.L<sup>-1</sup>. In order to extend its range of application, the calculation method of equilibrium constants must be reconsidered taking into account the non-ideal behaviors of gas and liquid phases. This requires more complete thermodynamics, as described in the next section.

### 3 Evolution of the model for HPHT conditions

At high pressure, the gas phase can not be considered as ideal and fugacity correction needs to be applied to account for interactions between gas molecules. As a consequence, three corrections must be applied in the solubility calculations leading to the ensemble Henry's law [11,12] (eq.1):

$$\gamma_i^{(x)} \cdot x_i \cdot H_i^{(x)}(T) \cdot \exp\left[\int (\nu_i^\infty / RT) \cdot dP\right] = \Phi_i P_i \quad (\text{eq. 1})$$

In this expression,  $x_i$  is the molar fraction of the component in the liquid phase,  $H_i^{(x)}(T)$  is the Henry's constant characterizing the solubility of the gas in water on the molar fraction scale and  $P_i$  is the partial pressure of component  $i$ . The activity coefficient defined on the molar fraction scale  $\gamma_i^{(x)}$  accounts for non-ideality of dissolved gas, the exponential term is known as the Poynting correction considering the effect of high pressures on the molar volume under infinite dilution and the fugacity coefficient  $\Phi_i$  corrects the gas phase for non ideal behavior.

Similarly, reactions in concentrated solutions are influenced by interactions between dissolved molecules and ions. To consider the non-ideal behavior of the liquid phase, the calculation of chemical equilibrium constants must also be corrected adding activity coefficients (eq.2).

$$K(T) = \prod_i (a_i)^{\nu_i} = \prod_i (\gamma_i^{(m)} \cdot m_i)^{\nu_i} \quad (\text{eq. 2})$$

In this expression,  $K(T)$  is the equilibrium constant of one of the chemical reactions (c) to (g),  $a_i$ ,  $m_i$  and  $\gamma_i^{(m)}$  are respectively the activity, the molality and the activity coefficient of component  $i$  (on the molality scale) in the liquid phase and  $\nu_i$  is the stoichiometric coefficient of component  $i$  for the chemical equilibrium considered.

For the specific application described in this paper, the Henry's constants  $H_i(T)$  are calculated using Dhima's correlations [13], the correlations allowing to describe equilibrium constants  $K(T)$  on a wide range of temperature are selected in the literature [14-18], fugacity coefficients in the gas phase are calculated using the Soreide and Whitson's model [19] and activity coefficients in the liquid phase are calculated applying Pitzer's model [20]. Each of these steps is presented in the next sections.

### Gaseous components fugacity coefficients

The Soreide and Whitson [19] modification of the Peng–Robinson equation of state (EOS) [21] is used for describing the fugacity of CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>O and CH<sub>4</sub> in the gas phase.

The Peng–Robinson EOS (eq.3) is derived from Van der Waals theory:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (\text{eq. 3})$$

In this expression, the pressure is calculated as a function of a repulsive term taking into account the co-volume  $b$  and a parameter  $a$  regarded as a measure of intermolecular attraction forces. This parameter depends on temperature.  $R$  is the gas constant,  $T$  is the temperature (K),  $P$  the total pressure (Pa) and  $v$  the molar volume (m<sup>3</sup>/mol).

Peng and Robinson used this equation to express the fugacity coefficient  $\Phi_i$  of a component  $i$  in a mixture [21].

$$\ln(\Phi_i) = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left( \frac{2\sum_j x_j a_{ji}}{a} - \frac{b_i}{b} \right) \ln \left( \frac{Z+2.414B}{Z-0.414B} \right) \quad (\text{eq. 4})$$

where  $A = \frac{aP}{R^2T^2}$ ,  $B = \frac{bP}{RT}$  and  $Z = \frac{Pv}{RT}$

In this expression,  $x_i$  is the molar fraction of component  $i$ ,  $b_i$  is the co-volume of component  $i$ ,  $a_{ji}$  characterizes the binary system formed by components  $j$  and  $i$ .

The presence of salts in the formation water also has a great influence on gas solubilities, which is not directly taken into account by the Peng and Robinson expression. Thus, Soreide and Whitson have proposed an extension of the Peng–Robinson EOS for treating the case of water–hydrocarbon mixtures in the presence of sodium chloride in the water phase. One of the main change consists in a modification of the attractive term of pure water.

Equations 4 was used in this study for the calculation of gas fugacities, using constant parameters values from reference [13].

### Activity coefficients in the liquid phase

The calculation of activity coefficients of components in the liquid phase was performed applying Pitzer's model [22] which derives from Debye–Hückel's method. This activity model is adapted to describe thermodynamic properties of concentrated brines solutions.

Debye–Hückel's equations give an expression of activity coefficients of ionic species from the ionic strength of the solution. This method takes into account long distance interactions between ionic species corresponding to electrostatic interactions. This approach is valid for slightly concentrated solutions (maximum molality of salts of about 1 mol / kg of water).

To adapt the activity model to highly concentrated brines, Pitzer has added short distance interaction terms to the Debye–Hückel's model corresponding to interactions between ionic species and the solvent. In the Pitzer's formalism,  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $\beta^{(2)}$  represent binary interaction parameters between ionic species and molecules and between cations and anions. Interactions between two cations or two anions  $\theta$  were neglected. Ternary interactions were also taken into account.  $C^\phi$  parameter refers to the interaction between two identical molecular or ionic species and a third different one, while  $\psi$  refers to the interaction between three different components. Table 1 summarizes all binary and ternary

parameters that we considered in our system, considering dissolved CO<sub>2</sub> and H<sub>2</sub>S and the following ionic species : Ca<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HS<sup>-</sup>, S<sup>2-</sup> and HO<sup>-</sup>.

**Table 1: References of Pitzer parameters used in this work**

Pitzer parameters $\beta^{(0)}$ , $\beta^{(1)}$ , $\beta^{(2)}$ , $C^\phi$ and $\psi$	Reference	Validity domain
H <sup>+</sup> / Cl <sup>-</sup>	[23]	273 K < T < 523 K, P < 400 bar
Ca <sup>2+</sup> / Cl <sup>-</sup>	[24]	298 K < T < 523 K
Ca <sup>2+</sup> / HCO <sub>3</sub> <sup>-</sup>	[25]	273 < T < 523 K, P < 1000 bar
Ca <sup>2+</sup> / CO <sub>3</sub> <sup>2-</sup>	[25]	273 < T < 523 K, P < 1000 bar
Ca <sup>2+</sup> / HO <sup>-</sup>	[26]	not reported
Na <sup>+</sup> / Cl <sup>-</sup>	[22]	273 K < T < 573K, P < 1000 bar
Na <sup>+</sup> / HCO <sub>3</sub> <sup>-</sup>	[27]	273 < T < 523 K
Na <sup>+</sup> / OH <sup>-</sup>	[28]	273 K < T < 623 K, P < 400 bar
Na <sup>+</sup> / CO <sub>3</sub> <sup>2-</sup>	[27]	273 < T < 523 K
Cl <sup>-</sup> / CO <sub>2</sub>	[29]	273 K < T < 533 K, P < 2000 bar
HCO <sub>3</sub> <sup>-</sup> / CO <sub>2</sub>	[30]	310 < T < 470 K
Ca <sup>2+</sup> / CO <sub>2</sub>	[25]	273 < T < 523 K, P < 1000 bar
Na <sup>+</sup> / CO <sub>2</sub>	[29]	273 K < T < 533 K, P < 2000 bar
Na <sup>+</sup> / H <sub>2</sub> S	[31]	298 K < T < 623 K
HS <sup>-</sup> / H <sub>2</sub> S	[32]	313 < T < 393 K, 100 bar
H <sub>2</sub> S / Na <sup>+</sup> / Cl <sup>-</sup>	[31]	298 K < T < 623 K
Ca <sup>2+</sup> / Cl <sup>-</sup> / CO <sub>2</sub>	[33]	T < 363 K
H <sub>2</sub> S / Na <sup>+</sup> / Cl <sup>-</sup>	[31]	298 K < T < 623 K
Ca <sup>2+</sup> / Cl <sup>-</sup> / CO <sub>2</sub>	[33]	T < 363 K
Na <sup>+</sup> / Cl <sup>-</sup> / CO <sub>2</sub>	[29]	273 K < T < 533 K, P < 2000 bar

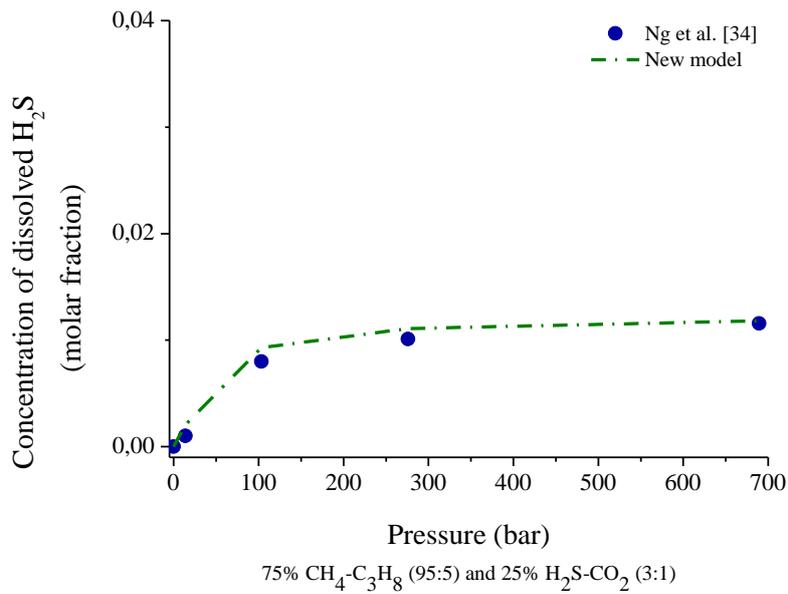
## 4 Results and discussion

### Solubility predictions

Once Soreide and Whitson's model and Pitzer's model provide respectively the fugacity and activity coefficients of components in the gas phase and in the liquid phase, the Ensemble Henry's law (eq. 1) is applied to assess the solubility of H<sub>2</sub>S and CO<sub>2</sub> in different conditions.

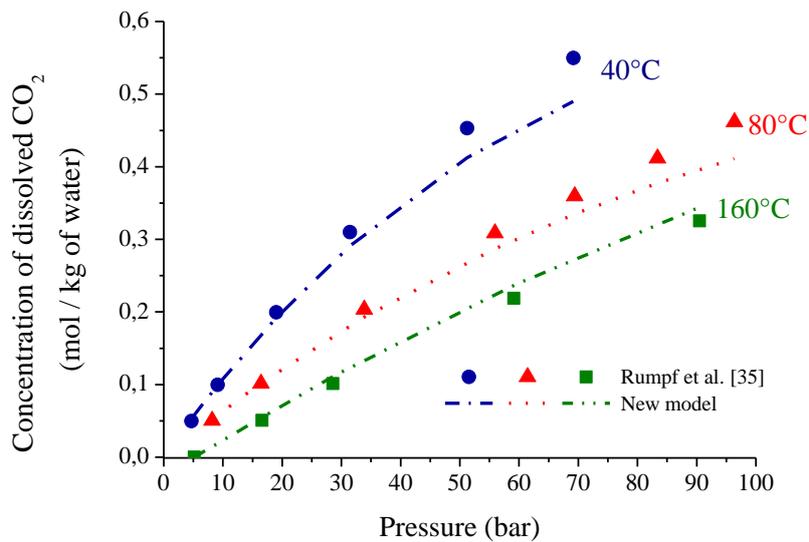
Note that in the proposed approach, we do not perform a rigorous thermodynamic flash calculation, since the fugacity equality constraint in both phases is not checked for water. It is a limitation of this actual approach, but the results presented further show that this approximation does not significantly affect the accuracy of the model in the considered temperature and pressure ranges.

The predictions for H<sub>2</sub>S solubility in water were compared to Ng et al. [34] experimental data. These authors performed measurements of H<sub>2</sub>S solubility in water in the case of different CH<sub>4</sub> / C<sub>3</sub>H<sub>8</sub> / H<sub>2</sub>S / CO<sub>2</sub> gas mixtures at various temperatures. Figure 1 shows the concentration of dissolved H<sub>2</sub>S versus the total pressure of 75% CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> (95:5 mole ratio) and 25 % H<sub>2</sub>S-CO<sub>2</sub>. The calculation of fugacity coefficients of gases was performed assuming propane to show similar interactions properties than methane with the others components. The new model gives excellent prediction of H<sub>2</sub>S with this set of experimental data.



**Figure 1: Predictions of H<sub>2</sub>S solubility in pure water under pressure of 75% CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> (95:5) and 25% H<sub>2</sub>S-CO<sub>2</sub> (3:1) gas mixture at 49°C.**

The new model predictions for CO<sub>2</sub> solubility in water were compared to Rumpf et al. [35] experimental data. These authors measured CO<sub>2</sub> solubility in highly concentrated NaCl solutions under pressure of pure CO<sub>2</sub> at different temperatures. Figure 2 shows the concentration of dissolved CO<sub>2</sub> in 4 mol.kg<sup>-1</sup> NaCl solution versus the total pressure at 40°C, 80°C and 160°C. Our new model also presents a good agreement with the experimental data, even in highly concentrated solution and on a wide range of temperature and pressure.



**Figure 2: Predictions of CO<sub>2</sub> solubility in NaCl 4 mol / kg of water at different temperatures**

For highly concentrated brine solutions, these results show that the application of the ensemble Henry's law combining Dhima's constants, Soreide and Whitson' model and Pitzer's model provides

accurate predictions of CO<sub>2</sub> and H<sub>2</sub>S solubilities even under high temperature, high pressure. It is therefore appropriate for in situ pH calculation, as detailed in the next part of the paper.

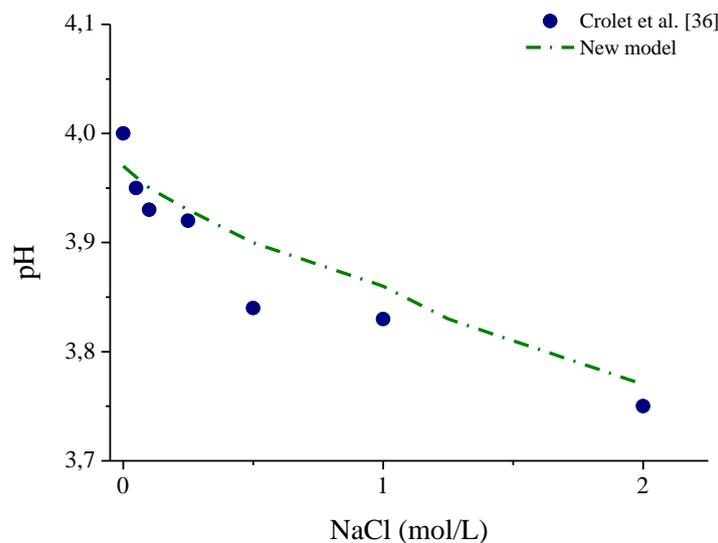
### pH predictions

The calculation method of pH is classically derived from the electroneutrality equation as described elsewhere [36]. Once H<sup>+</sup> concentration is determined, pH is calculated from H<sup>+</sup> activity according to :

$$pH = -\log a_{H^+} = -\log(\gamma_{H^+}^{(m)} \cdot m_{H^+}) \quad (\text{eq. 6})$$

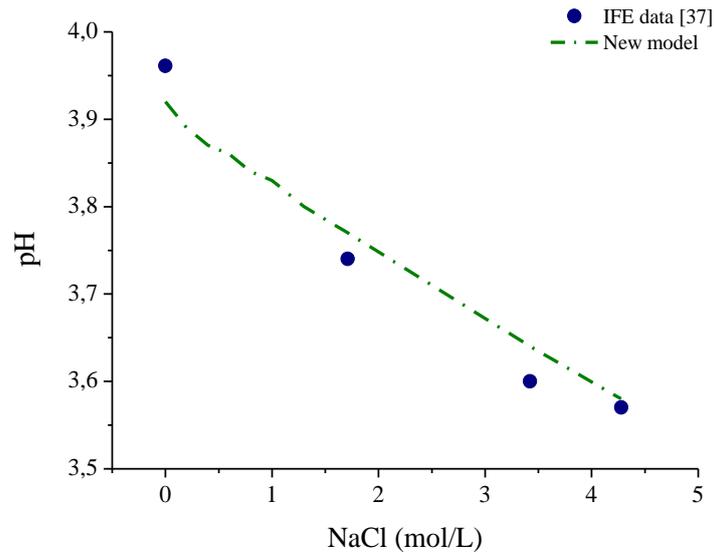
In this expression,  $a_{H^+}$  is the activity of H<sup>+</sup>,  $\gamma_{H^+}^{(m)}$  is the activity coefficient of H<sup>+</sup> on the molality scale and  $m_{H^+}$  is the concentration of H<sup>+</sup> in mol / kg of water.

Comparisons with different sets of experimental data are presented from Figure 3 to Figure 5. Crolet and Bonis [36] reported pH measurements under 1 bar of H<sub>2</sub>S at 25°C and for different sodium chloride concentrations. Our model presents an excellent correlation with the experimental data up to 2 mol.L<sup>-1</sup> NaCl (Figure 3).



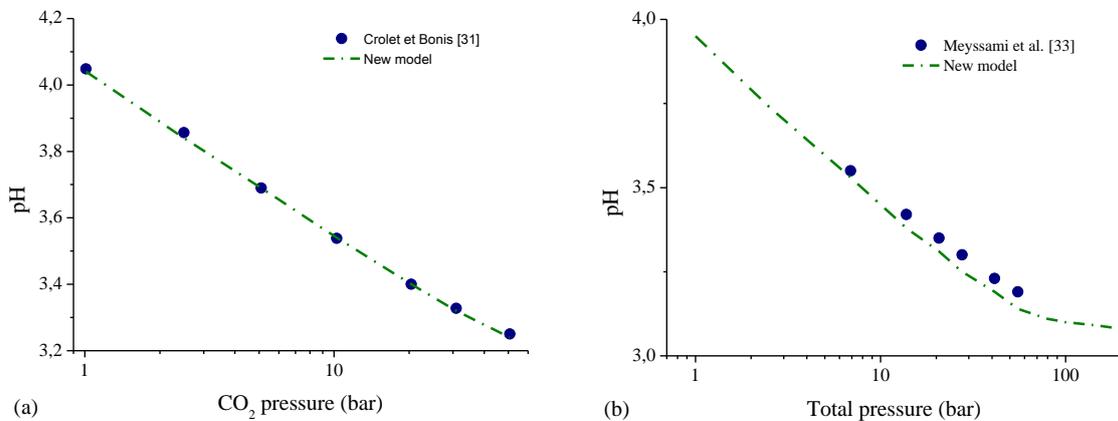
**Figure 3: Influence of NaCl concentration on pH at 25°C under 1 bar of H<sub>2</sub>S**

Another set of experimental data for highly concentrated solutions was proposed by Hinds et al. [37], at 1 bar CO<sub>2</sub> and 25°C. As illustrated in Figure 4 the new model predicts the experimental results within less than 0,05 pH unit in the whole range of ionic strength from zero to more than 4 mol.L<sup>-1</sup> NaCl.



**Figure 4: Influence of NaCl concentration on pH at 25°C under 1 bar of CO<sub>2</sub>**

Validity of the new model at high pressure and temperature was evaluated from measurements by Crolet and Bonis [36] and Meysami et al [38]. Figure 5.a illustrates measurements performed at 74°C in 0.5 mol.L<sup>-1</sup> NaCl solutions. Figure 5.b presents measurements in pure water at 32°C. For both applications, an excellent prediction is obtained up to 50 bar of CO<sub>2</sub>.



**Figure 5: Influence of CO<sub>2</sub> pressure on pH (a) at 74°C in NaCl 0.5 mol.L<sup>-1</sup> [36] and (b) at 32°C in pure water [38].**

## 5 Conclusion

The in-situ pH of formation water is one of the most important parameters for material selection in the oil and gas production. Most predictions tools currently employed 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).

However, the increasing interest of HPHT fields requires more accurate models with extended validity domain. For this purpose, we applied a calculation method based on the ensemble Henry's law for

solubility calculations and taking into account the activity of chemical species for chemical equilibrium constants calculation.

The impact of high pressures on gas solubility was considered by fugacity coefficients calculation using Soreide and Whitson's model. The effect of high concentrations of salts on the activity of chemical species in the liquid phase was modeled using Pitzer's formalism.

Even though only sparse experimental data is available in the literature at high temperature, high pressure and in concentrated solutions, all comparisons between the new model and the measurements gave an excellent agreement. Due to the lack of experimental data for temperatures above 75°C and pressures higher than 50 bar, the validity of our model was not checked in these conditions. However considering the validity domains of individual elements of the model taken from the literature, we expect accurate predictions of in-situ pH in highly concentrated brines (up to 5 mol/L) under high pressure (around 1000 bar) and high temperature (to 250°C). This represents a considerable improvement of the actual tools, typically limited to 150°C and 50 bar.

## Nomenclature

$P_i$	partial pressure of gas i (Pa)
$S_i$	solubility constant of component i
$K_{hyd}$	equilibrium constant of CO <sub>2</sub> hydration
$K$	equilibrium constant of H <sub>2</sub> CO <sub>3</sub> first dissociation
$K_2$	equilibrium constant of H <sub>2</sub> CO <sub>3</sub> second dissociation
$K_1'$	equilibrium constant of H <sub>2</sub> S first dissociation
$K_2'$	equilibrium constant of H <sub>2</sub> S second dissociation
$\gamma_i^{(x)}$ and $\gamma_i^{(m)}$	activity coefficient of component i on the molar fraction scale and on the molality scale
$x_i$	molar fraction of component i
$H_i^{(x)}(T)$	Henry constant defined in the molar fraction scale (Pa)
$R$	ideal gas constant (J.mol <sup>-1</sup> .K <sup>-1</sup> )
$T$	temperature (K)
$v_i^\infty$	molar volume under infinite dilution (m <sup>3</sup> /mol)
$\Phi_i$	fugacity coefficient of component i
$a_i$	activity of i in the liquid phase
$\nu_i$	stoichiometric coefficient of i
$m_i$	molality of i (mol / kg of water)
$v$	molar volume (m <sup>3</sup> .mol <sup>-1</sup> )
$a, b, a_{ij}, b_i$	parameters used in Peng and Robinson equation of state
$\beta^{(0)}, \beta^{(1)}, \beta^{(2)}, C^\phi, \psi$	Pitzer's model parameters

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