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## Estimation of pH in Oil and Gas Production Environments

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### ABSTRACT

One of the important parameters in controlling corrosion in the oil and gas industry is pH. The pH affects both the electrochemical reactions and the formation of surface layers. Various parameters, including the concentrations of sulphate, bicarbonate, and acetate ions; the partial pressures of acid gases ( $\text{CO}_2$  and  $\text{H}_2\text{S}$ ); and temperature affect the pH. Further presence of some species may buffer the pH. In this paper, the theory of pH calculations, methods of determining pH, and models used for predicting pH, as well as precautions in using pH values for corrosion control have been reviewed.

### INTRODUCTION

Oil and gas production environments contain acid gases carbon dioxide [ $\text{CO}_2$ ] (sweet) and hydrogen sulfide [ $\text{H}_2\text{S}$ ] (sour). Dissolution of these acid gases in the produced or formation waters decreases the pH and is accompanied by an increase in corrosivity. It is normally assumed that the rate of dissolution of acid gases is proportional to their respective partial pressures ( $\text{pCO}_2$  and  $\text{pH}_2\text{S}$ ).

Based on the examination of nineteen parameters from gas condensate wells it was found that pH is by far the most significant parameter determining corrosivity<sup>1</sup>. Because partial pressures of both  $\text{H}_2\text{S}$  and  $\text{CO}_2$  produce the same effect, i.e., they decrease pH, the total partial pressures of the acid gases is considered acidity for estimating pH. If acid gas partial pressure is less than 0.1 psi, the pH is assumed to close to neutral (pH 7). In terms of the relation between pH and corrosion, diverse groups have reported different results.

In sweet medium:

- Schmitt et al. found that between pH 4 and 7 and at temperatures of 20, 40, 60, and 80EC, the protective carbonate layers are formed only at pH above 5. At temperatures above 50°C, the layers are sometimes ineffective in reducing the corrosion rates of carbon steels, even at pH values as high as 6.0<sup>2, 3</sup>.
- Mishra et al., based on tests carried out at  $\text{CO}_2$  partial pressure of 0.002 MPa, found that

FeCO<sub>3</sub> was formed at pH of 6.5 whereas oxides/hydroxides were formed at pH 8.5<sup>4</sup>.

- Xia et al detected Fe(HCO<sub>3</sub>)<sub>2</sub> on steel specimens immersed in solution of pH between 5.4 and 6.2, whereas FeCO<sub>3</sub> was detected between pH 7 and 8.<sup>5</sup>
- Simpson et al found FeCO<sub>3</sub> in the corrosion layer at pH<9.5 and at temperatures below 50°C<sup>6</sup>.
- Even though ferrous materials generally have been regarded as exhibiting a low susceptibility to corrosion at pH values above 10, Legrand et al found that for C4140 (UNS G41400), increasing the temperature to 60°C at pH 10 increased the overall corrosion rate by about 20 to 100 times compared with the rate at room temperature and that addition of potassium bicarbonate/potassium carbonate (KHCO<sub>3</sub> / K<sub>2</sub>CO<sub>3</sub>) significantly reduced the corrosion rate<sup>7</sup>.
- Adamy et al. found that the influence of temperature on corrosion rate at pH values of 11 to 13 was very minor<sup>8</sup>.
- Dugstead has proposed controlling CO<sub>2</sub> corrosion by controlling pH<sup>9</sup>.

In sour medium<sup>10</sup>:

- Shoesmith et al. found mackinawite (tetragonal FeS<sub>(1-X)</sub>) at pH 7 and cubic ferrous sulfide and troilite between pH 3 and 5. The corrosion rate increased with decreasing pH.<sup>11</sup>
- MacDonald on the other hand found least protective (mackinawite) being formed when the pH of the medium is between 6.5 and 8.8. Outside this range, protective scales of pyrrhotite and/or pyrite are formed.<sup>12</sup>
- Craig observed combinations of pyrite, troilite, and mackinawite as surface layers when the pH was varied in the range from 4 to 6.3. Tetragonal FeS is initially formed on wet steel in the presence of H<sub>2</sub>S–O<sub>2</sub> mixtures at an approximate pH of 5.5 and ambient temperature. Oxidation of this product to iron oxide and elemental sulphur resulted in the increased corrosion rate<sup>13</sup>. Below 0.1 psia of H<sub>2</sub>S, a surface layer consisting of pyrite, FeS<sub>2</sub>, troilite, hexagonal FeS, mackinawite and Fe<sub>(1+x)</sub>S is formed on the surface. When the concentration of H<sub>2</sub>S is between 0.1 and 4 psia, a nonprotective surface layer composed of troilite, pyrite, and a predominant amount of mackinawite is formed. From 0.1 to 4.0 psia, the corrosion rate increases with increasing H<sub>2</sub>S partial pressure, i.e., corrosion rate increases with decreasing pH.
- Sardisco found that the sulfide layer is unprotective in the pH range 6.5 to 8.8. At this pH range mackinawite<sup>14</sup> and HS<sup>-</sup> are the predominant corrosion products.
- MacDonald et al. found no corrosion products at high (above 9) and low (less than 2) pH solutions, but between pH 2 and 9, corrosion occurred with the formation of iron sulphide layers.<sup>12</sup>

- Gupta et al found the general corrosion rates to be higher at lower pH and at all sulfide ion levels studied. At low pH values, the corrosion rates increase with increasing sulfide concentrations. At sulfide concentrations in the range of 150 to 500 mg/L, carbon steel is susceptible to pitting corrosion.<sup>15</sup>
- Smith thoroughly reviewed the state-of-the-art on current understanding of sour corrosion in oil and gas industry including the effect of pH<sup>16</sup>.

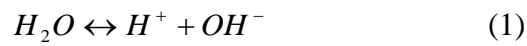
Despite vast amount of knowledge on relationship between pH and corrosion rate, the estimation of pH in the oil and gas industry is not clearly documented. Practices of estimating pH include:

- Use of computer simulated models (developed either using fundamental first principles or using data generated in the laboratory tests)
- Measure of pH after withdrawing samples from the environment (often not accounting for the loss of acid gases), and, rarely, in-situ measure of pH.

The objectives of this paper are to review theoretical aspects of pH, methods of determining pH, and models used in the oil and gas industry for predicting pH, and precautions to be exercised in using pH value in corrosion control.

### **THEORETICAL ASPECTS OF pH**

Water exists in equilibrium between the molecular and ionic forms as expressed by:



Where  $H^+$  is the hydrogen ion and  $OH^-$  is the hydroxyl ion.

The equilibrium constant or ionization constant of water ( $K_w$ ) is expressed as:

$$[H^+][OH^-] = K_w = 1.00 \cdot 10^{-14} \quad (2)$$

To meet the charge balance in pure water the concentration of hydrogen ion and hydroxyl ion must be equal:

$$[H^+] = [OH^-] \quad (3)$$

From Eqns. 2 and 3 we then have:

$$[H^+] = 1.00 \cdot 10^{-7} \quad (4)$$

$$[OH^-] = 1.00 \cdot 10^{-7} \quad (5)$$

Concentrations of solutions are mostly less than one mole per liter; consequently, the logarithm of concentration is mostly a negative number. Because it is easy to work with positive number, a method in which lower case “p” is used as abbreviation to indicate “take the negative logarithm

of". Thus, the concentration of hydrogen ion may be conveniently expressed as:

$$pH = -\log_{10}[H^+] \quad (6)$$

In theory, pH is defined as the negative logarithm of the activity of hydrogen ion<sup>17</sup>:

$$pH = -\log_{10}[H^+]\gamma_{H^+} \quad (7)$$

Where  $\gamma_{H^+}$  is the activity coefficient of hydrogen ion and is a measure of the inter-ionic forces. For most practical conditions, the activity coefficient of hydrogen ion is assumed to be unity so that Eqn. 6 is frequently used than Eqn. 7 to define pH.

The concentrations of hydroxyl ions can similarly be defined:

$$pOH = -\log_{10}[OH^-] \quad (8)$$

For pure water is thus given as:

$$pH + pOH = 14 \quad (9)$$

Pure water is defined as neutral on acid-base scale. If the concentration of hydrogen ion is larger than that of hydroxyl ion, the solution is acidic and if the concentration of hydrogen ion is smaller than that of hydroxyl ion, the c solution is basic.

Species that dissolve to furnish hydrogen ions are known as acid and that dissolve to furnish hydroxyl ions are known as base. The pH of pure water changes not only on the dissolution of species but also on the extent of their dissociation in the solution.

### Solubility

When ionic species dissolve in pure water two conditions must be satisfied: mass balance and charge balance. For example, if a salt of formula MX dissolves in water to form a saturated solution, then, assuming the charge on ionic species is univalent then the mass-balance and charge-balance are established as:

$$[M^+] = S = [X^-] \quad (10)$$

Where  $[M^+]$  is the concentration of cation and  $[X^-]$  is the concentration of anion, and S is the number of moles of MX in the solution.

The solubility of ionic species may commonly be represented by "solubility product" ( $K_{sp}$ ) as:

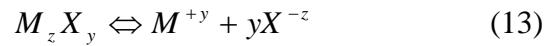
$$K_{sp} = [M^+].[X^-] \quad (11)$$

So that:

$$S = \sqrt{K_{sp}} \quad (12)$$

Thus, the solubility of an ionic species in pure water depends on the solubility product alone.

For species for which the charges on the ions are not equal the dissolution may be represented as:



Where y and z are charges on cation and anion, respectively. The solubility product ( $K_{sp}$ ) for Eqn. 13 is given as:

$$K_{sp} = [M^{+y}]^z \cdot [X^{-z}]^y \quad (14)$$

W. Nernst proposed Eqn. 14. Dissolution of one mole of  $M_z X_y$  produces z moles of cations and y moles of anions so that:

$$[M^{+y}] = zS \quad (15)$$

$$[X^{-z}] = yS \quad (16)$$

Combining Eqns. 14, 15, and 16 will produce:

$$K_{sp} = (zS)^z \cdot (yS)^y \quad (17)$$

so that:

$$S = \sqrt[z+y]{K_{sp} / z^z y^y} \quad (18)$$

The solubility estimated from solubility product must be corrected to account for common ion effect, activity coefficient, hydrolysis, and presence of complexing agents.

### Common Ion Effect

The solubility of chemical species decreases in the presence of common ions. As an example, the solubility barium sulphate ( $BaSO_4$ ) is more in pure water than in water containing either barium chloride ( $BaCl_2$ ) or sodium sulphate ( $Na_2SO_4$ ). This effect is known as common ion effect. This happens because addition of  $BaCl_2$  increases the concentration of  $Ba^{2+}$  in the solution; consequently, the  $Ba^{2+}$  from dissolution of  $BaSO_4$  must decrease to maintain the chemical equilibrium. Similarly, addition of  $Na_2SO_4$  increases the concentration of  $SO_4^{2-}$  in the solution; consequently, the  $SO_4^{2-}$  from the dissolution of  $BaSO_4$  must decrease. Therefore, in the presence of common effect, the solution concentration of species can not be estimated from the solubility

product alone.

### Activity Coefficient

In some situations, the solubility of species may increase in the presence of other ions. This increase is due to inter-ionic forces. The inter-ionic forces occur only in the concentration solutions and activity coefficient is used to account for inter-ionic forces. The activity coefficient of single ion can not be determined because one cannot isolate individual ions. For this reason, the activity coefficient of salt solution ( $\gamma$ ) is given as:

$$\gamma = \sqrt{\gamma_+ \gamma_-} \quad (19)$$

Where  $\gamma_+$  is the activity coefficient of cation and  $\gamma_-$  is the activity coefficient of anion.

The activity coefficient is a function of the ionic strength (I) of the solution. The ionic strength of the solution is defined as:

$$I = \frac{1}{2} \sum_i C_i z_i^2 \quad (20)$$

Where C is the concentration of ion, z is the charge on ion, and i is the number of ions in the solution.

Debye-Huckel developed theory derived the relationship between ionic strength and activity coefficient as:

$$\log_{10} \gamma = -0.509 \sqrt{I} \quad (21)$$

In the absence of inter-ionic effects, the activity coefficient becomes unit which occurs in very dilute solution.

### Hydrolysis

In many instances the dissolution of ionic species in acidic solution is higher than that in pure water. This happens due to hydrolysis. Though theoretical treatment of this issue is complex and beyond the scope of this review paper, it can qualitatively be inferred that anion hydrolysis is extensive in acid solutions and cation hydrolysis is extensive in basic solutions. Both effects tend to remove the ions of the salt from the solution, thereby increase the solubility of the salt over the value estimated from solubility product alone.

### Complex formation

The solubility of ionic species in the presence of another species may initially decrease and then may increase. The increase of solubility at higher concentration is due to formation of chemical complex.

## Ionisation

Solubility product (corrected for other effects) defines the extent of dissolution of an ionic species in water. The extent to which the dissolved ions dissociate determines their influence on pH. The dissociation of an ionic species in water may be represented as:



The extent of dissociation is defined by ionisation constant,  $K_a$ :

$$K_a = \frac{[H^+] + [A^-]}{HA} \quad (23)$$

- Ionic species that completely dissociate are known as strong acids. The ionisation constant for strong acids is greater than unity
- Species that do not dissociate at all are known as weak acids. The ionisation constant for acids that do not dissociate at all is typically lesser than  $10^{-14}$ .
- Ionic species that partially dissociate have ionic constant between  $10^{-1}$  and  $10^{-14}$ .

Because most ionisation constant values are less than unity, the ionisation constant is also represented as (like hydrogen ion concentration (see Eqn. 6)):

$$pK_a = -\log_{10} .K_a \quad (24)$$

For polyprotic acids, i.e., acids that can produce two or more protons on ionisation, there are two or more ionisation constants. Common polyprotic acids encountered in oil and gas production environments are carbonic acid ( $H_2CO_3$ ) and hydrogen sulphide ( $H_2S$ ).

When  $CO_2$  dissolves in water it produces carbonic acid. However, the hydration of  $CO_2$  is slow (about 0.1 second) when compared to dissociation of  $H_2CO_3$  to bicarbonate ion (which takes place within  $10^{-6}$  second). For this reason, the first ionisation constant of carbonic acid ( $K_{a1}$ ) corresponds to the following reaction:



The second ionisation constant ( $K_{a2}$ ) corresponds to the following reaction:



Table 1 lists ionisation constants of species.

## Buffer effect

In the presence of weak acid and its conjugate base (i.e., the one that does not enter the reaction), the pH does not vary due to buffering action. In buffer solution, if hydrogen ions are produced,

they react with the conjugate base to produce acid and if hydrogen ions are consumed, the weak acid dissociates to produce more hydrogen ions. The net result is that the pH does not change substantially. A common buffer causing agent in the oil and gas industry is the presence of acetic acid and sodium acetate. The pH of solution containing 0.01 molar acetic acid and 0.01 molar sodium acetate is buffered at 4.75. To this solution addition of 0.001 mole of hydrochloric acid changes the pH to 4.67. On the other hand, addition of same concentration of HCl to pure water changes the pH from 7.0 to 3.00.

## METHODS FOR MEASURING pH

Fabrication of pH probes and using them to measure pH has been well established and are briefly presented in this section. pH is in practice measured based on the following principle:

$$E = E_o - \frac{2.303RT}{F} \cdot pH \quad (27)$$

Where E is the electrode potential,  $E_o$  is the standard electrode potential, R is the gas constant, T is the temperature, and F is Faraday constant. The variation of potential of glass electrode is measured using the reference electrode.

The fabrication of pH probe has not fundamentally changed for over 60 to 70 years. Typical components of pH probe are presented in Fig. 1. Most commonly glass electrode is used as pH probe. The pH measured is a function of pH meter. In order to make reliable measurement the pH meter must be calibrated at several pHs using standard buffer solutions. It is also assumed that the pH of these buffer solutions has been theoretically calculated. When the pH meter is not in used, it should be properly stored so that the pH sensitive electrode does not dry out. Specific procedures for storing depend on the type of pH meter and should be strictly followed.

The measured pH depends on several parameters including reliability of calibration, variation of temperature, range in which the pH is measured, and interfering species. The pH range in which the pH meter is reliable should be established. Using pH beyond the range in which the pH meter is reliable leads to acidic range error and basic range error:

- At higher concentration of hydrogen ions (typically at pH values lower than one), dependence of electrode potential on pH becomes non-linear. In this range, the influence of anions becomes appreciable.
- At lower concentration of hydrogen ions (typically at pH values higher than 12), dependence of electrode potential on pH again becomes non-linear. In this range, the influence of alkali metal (such as lithium, sodium, and potassium) ions becomes appreciable.

pH probes are also commercially available to measure pH under higher temperature and higher pressure. The pH can be measured online in process streams using pressure- fitted pH probe that is connected using mounting gland.

Recently, attempts have been made to develop pH probes using materials other than glass electrodes. Some of them are described in the following paragraphs.



### Metal Electrode pH Sensor

A miniaturized (with diameter less than 150  $\mu\text{m}$ ) iridium-iridium oxide (IIO) pH probe with comparable performance to glass electrode has been developed<sup>18</sup>. This pH probe responds linearly with pH in the range 2 and 12. The variation of potential measured by the probe is about 50 mV per pH 9 in this range. Though the potential measured with this electrode varies by about 200 mV between measurements, unlike glass electrode this electrode does not require calibration before each measurement. The primary application of IIO pH probe is the ability to measure pH in a small volume of solution in droplets, crevices, and scratches as well as thin layer of water on top of materials.

Zirconia is extensively used as a pH sensor in high-temperature (above 500°C) and high-pressure (above 5,000 psi) applications. The potential response of the electrode to pH is rapid. A metal electrode is placed in ceramic tube for high pressure application. Teflon and brazing materials are used to provide effective seal<sup>19,20</sup>.

pH sensor using niobium-doped titanium oxide ( $\text{TiO}_2$ ) has been successfully used to measure pH at higher temperature (298 to 523 K). The pH response of the sensor is based on Nernst equation. The sensor response is fast, stable, and not affected by redox systems in the solutions. However, presence of higher concentrations (above  $10^3 \text{ mol/m}^3$ ) of sodium and potassium ions interfered with the sensor response<sup>21</sup>.

Stainless steel electrode has also been demonstrated to effectively function as pH sensor in the range 1 to 13 pH. The response time is short (less than 3 sec). The sensor response is not affected by the presence of alkali-metal ions, ammonium ion, and other cations; however, the presence of chloride ion affects the pH sensor response<sup>22</sup>.

pH sensor using iridium oxide on iridium electrode has also been demonstrated. This sensor is not affected by the presence of sulphate and sulphide ions; however, presence of bisulphate and thiosulphate ions interfered with the response of the sensor<sup>23</sup>.

pH sensor has also been demonstrated using molybdenum oxide coated molybdenum wires. The pH sensor responses linearly to pH in the range 2 and 12 and is not affected by halide ions<sup>24</sup>.

### Calorimetry pH Sensors

Chemicals changing color with pH have been extensively used for measuring pH. These chemicals are entrapped in polymeric matrix and applied on surface on which the pH change needs to be measured. Many of these studies have pointed out that the range in which the pH sensors are sensitive changes somewhat upon entrapment. Table 2 presents properties of some pH sensors<sup>25</sup>. This change in behavior must be accounted for when using calorimetry pH sensors that are entrapped in polymer matrix.

### Fluorescent pH Sensors

Chemicals producing fluorescent have also been used in limited manner for measuring pH in specific applications. For example, a study on using modified paint system to detect buried crevice corrosion in the underlying metal successfully used coumarin and 7-hydroxycoumarin as fluorescent materials as pH sensor beneath paints<sup>26</sup>.

pH sensor has also been demonstrated by attaching the fluorescent chemical (e.g., fluorescein isothiocyanate isomer I (FITC)) onto fiber optic cable. The pH sensor range depends on the type of chemical and with FITC the sensor is sensitive in the pH range 5.0 and 7.5<sup>27</sup>.

### MODELS TO PREDICT pH IN OIL AND GAS PRODUCTION ENVIRONMENTS

Actual measurement of pH in the field operating conditions of higher pressure is difficult. For this reason, pH is often measured under atmospheric pressure conditions. However, when the pressure is reduced the acid gases often escape resulting in pH value higher than happens under the oil and gas production conditions. This pH value leads to under estimation of corrosion rate. For this reason, theoretical and empirical models have been developed to predict pH in oil and gas production environments. In this section the models to predict pH in oil and gas production environments are reviewed.

#### Crolet and Bonis Model<sup>28-31</sup>

Crolet and Bonis developed a pH model considering the effects of acetic acid, propionic acid, acetate ion, bicarbonate, calcite (CaCO<sub>3</sub>) and carbonic acid. Initially they developed an equation considering the main ionic species reported in production waters. According to their first model:

$$\frac{K_s}{K_1 K_2 P} H^{+4} + \left(1 + \frac{K_a K_s}{K_1 K_2 P}\right) H^{+3} + (K_a - \lambda + A_{co}^-) H^{+2} - (K_1 P + K_a \lambda) H^+ - K_1 K_a P = 0 \quad (28)$$

Where  $K_s$  is the solubility product of calcite,  $K_a$  is the dissociation of acetic acid,  $K_1$  is the dissociation of carbonic acid,  $K_2$  is the second dissociation of carbonic acid,  $P$  is the fugacity of CO<sub>2</sub>, and  $\lambda$  is a factor used to represent the lack of acetate and is defined as:

$$\lambda = \lambda' + A_{co}^- \quad (29)$$

Where  $\lambda'$  is Poirier's parameter and  $A_{co}^-$  is the concentration for acetate given by the water is considered as the reference state.

For simple cases they used asymptotic laws to predict pH as:

$$pH_w = \frac{1}{2} pK_1 - \frac{1}{2} \text{Log}P \quad (30)$$

where  $K_1$  is the first dissociation of carbonic acid in water exposed to CO<sub>2</sub> and  $P$  is the fugacity of CO<sub>2</sub> (expressed as partial pressure in MPa).

In order to validate their prediction, Crolet and Bonis carried out experiments at elevated pressure using solutions containing NaCl, CaCO<sub>3</sub> and acetate (in the form of sodium acetate). They used pH meter to measure pH. The pH predicted agreed well with measured pH.

Based on the prediction, experimental data, and analysis of produced water from forty different wells the authors built a conversational program to calculate the pH of produced water. The inputs for the program are water composition (including acetates, other organic acid anions, bicarbonates, chlorides, sulphates, sodium, potassium, and magnesium), partial pressure of CO<sub>2</sub>, gas composition, and temperature. Based on the inputs the program calculates pH the pH at various locations in the wells considering solubility equilibrium, dissociation of species, and electrical neutrality of ionic species in solution.

### Garsany, Pletcher and Hedges Model<sup>32</sup>

Garsany et al used a commercial software program to predict the pH of 3% NaCl brine containing different concentrations of CO<sub>2</sub> and acetic acid. The software program used the dissociation constant, and the mean ionic activity constant of the species dissolved in the brine solution to predict pH. The predicted pH was confirmed with pH Meter and good agreement was found between the experimentally observed and calculated pH. The authors further noted that increasing the acetate concentration led to an increase in pH.

### Kaasa and Østvold Model<sup>33, 34</sup>

Kaasa et al developed a model to predict pH and mineral scaling in water containing CO<sub>2</sub> and H<sub>2</sub>S at temperature between zero and 200°C and at pressures between 1 and 500 bar. The core equation of their model is an equation that describes the alkalinity in a 3-phase (Gas, Oil, and water):

$$A_T = \frac{n_{CO_2}^{tot} \cdot P \cdot \left[ K_H(CO_2) \frac{K_1(CO_2)}{m_{H^+}} \left( 1 + 2 \frac{K_2(CO_2)}{m_{H^+}} \right) \right]}{NO/K_{CO_2} + NG + P \cdot M_{CO_2}(H^+)} + \frac{n_{H_2S}^{tot} \cdot P \cdot \left[ K_H(H_2S) \frac{K_1(H_2S)}{m_{H^+}} \right]}{NO/K_{H_2S} + NG + P \cdot M_{H_2S}(H^+)} + \frac{m_{HAc}^{tot} K_{HAc}}{m_{H^+} + K_{HAc}} + \frac{K_W}{m_{H^+}} - m_{H^+} \quad (31)$$

Where  $M_{H_2S}(H^+)$  is the water phase mass balance function for H<sub>2</sub>S;  $M_{CO_2}(H^+)$  is the water phase mass balance function for CO<sub>2</sub>, NO is the total number of moles in the oil phase; NG is the total number of moles in the gas phase; and  $m_i$  is the molality (mole/kg H<sub>2</sub>O) of species (HAc, H<sub>2</sub>S and CO<sub>2</sub>),  $n_{CO_2}^{tot}$  is the total number of moles of CO<sub>2</sub>,  $n_{H_2S}^{tot}$  is the total number of moles of H<sub>2</sub>S,  $K_{CO_2}$  is the Gas-Oil equilibrium constant for CO<sub>2</sub>,  $K_{H_2S}$  is the Gas-Oil equilibrium constant for H<sub>2</sub>S,  $K_H(CO_2)$  is the Gas-Water equilibrium constant for CO<sub>2</sub>,  $K_1(CO_2)$  is the first dissociation constant for CO<sub>2</sub>,  $K_2(CO_2)$  is the second dissociation constant for CO<sub>2</sub>.  $K_1(H_2S)$  is the first dissociation constant of H<sub>2</sub>S,  $K_W$  is the dissociation constant of water,  $K_{HAc}$  is the dissociation constant of acetic acid and P is the total pressure in bar.

When a water phase is present, there is also a vapour pressure of water, independent of the oil and gas compositions. The water activity is calculated at various temperatures and pressures. The water activity is then combined with the vapour pressure of pure water to calculate the fugacity of water. Dividing the fugacity by the total pressure and the fugacity coefficient gives the mole fraction of water in the gas phase. The iteration routine is then used to calculate mole fraction of water in water and vapour phases.

When the mole fraction of water has been calculated, it is regarded as a constant, and the mole

fractions of all the other hydrocarbons are then determined by solving:

$$F(G) = \sum_i y_i - \sum_i x_i + y_{H_2O} = \sum_i \frac{z_i(K_i - 1)}{1 + G \left( \frac{K_i}{1 - y_{H_2O}} - 1 \right)} + y_{H_2O} = 0 \quad (32)$$

Where G is the gas fraction defined as  $G = NG / (NG + NO)$ . NG+NO is the number of moles of all hydrocarbons in a system containing 1 kg water. F(G) is monotonically decreasing and a root  $0 < G < 1$  exist provided.  $z_i$  is the mole fraction of species i in the hydrocarbon phase,  $x_i$  is the mole fraction of species i in the oil phase and  $y_{H_2O}$  is the mole fraction of water in the gas phase.

An estimate of  $K_i$  (equilibrium constant of species i) is made at the beginning using:

$$K_i = \frac{1}{P_{ri}} \exp \left[ 5.3727(1 + \omega_i) \left( 1 - \frac{1}{T_{ri}} \right) \right] \quad (33)$$

Where  $P_{ri}$  is the reduced pressure of species i in bar  $T_{ri}$  is the reduced temperature of species i in Kelvin and  $\omega$  is the acentric factor of species i.

The  $K_i$  values should fulfil the following requirements to simplify the calculation.

$$\sum_i K_i Z_i > 1 - y_{H_2O} \quad \text{and} \quad \sum_i \frac{Z_i}{K_i} > 1 + \frac{y_{H_2O}}{1 - y_{H_2O}} \quad (34)$$

The mole fractions of all species in the liquid and the gas phase and the alkalinity are then solved using a stepwise iterative technique by assuming that all the hydrocarbons,  $CO_2$  and  $H_2S$  are present in the hydrocarbon phase. From the calculation, the relative amounts of gas, and NO and NG are calculated. Once the values of NO and NG are known the alkalinity equation is solved with respect to  $m_{H^+}$ . The values of  $m_{H^+}$  are then used to obtain the pH in complex and multiple iteration calculations. A program has been developed to calculate pH.

### Miyasaka Model<sup>35</sup>

Miyasaka determines that when the sulfate content in a solution is negligible, typically less than  $10^{-2}$  Mol., the pH buffering effect of sulfate can be ignored. In the equation of Miyasaka the second dissociation of  $H_2S$  and  $CO_2$  is also disregarded because the pH region of concern is an acid region.

The basic general equation used by Miyasaka is the following :

$$m_{H^+}^3 + (m_{CO_2} + m_{HCO_3^-} + C_2)m_{H^+}^2 - (C_1 m_{H_2S} + C_3)m_{H^+} - C_2(C_1 m_{H_2S} + C_3) = 0$$

Where

$$K_{1,H\gamma H_2S / \gamma^2 \pm H_2S} = C_1$$

$$K_{1,C\gamma CO_2 / \gamma^2 \pm CO_2} = C_2$$

$$K_{w, / \gamma^2 \pm H_2O} = C_3$$

$$K_{1,S\gamma HSO_4^- / \gamma^2 \pm HSO_4^-} = C_4$$

And

$m_i$  is molar concentration of i chemical (mol/kg-H<sub>2</sub>O)

$K_{1,i}$  is first dissociation constant of i chemical

$K_w$  is dissociation of water

$\gamma_i$  is activity coefficient of i chemical

$\gamma_{\pm i}$  is mean activity coefficient of i chemical

The true  $m_{H^+}$  are the positive solutions of the equation. The  $m_{H^+}$  value was calculated by the author by either the theoretical solutions for a quadratic equation or numerical solutions by the Newton's method.

Then once  $m_{H^+}$  is known it is easy to estimate the value through this well know equation.

$$pH = -\log \gamma_{H^+} m_{H^+}$$

Resolving quadratic equation is not an easy task and need the assistance of sophisticated calculation software. Moreover, this equation cannot be used if some organic acids are present in the tested waters.

#### NACE Model<sup>36</sup>

The purpose of that standard is to give requirements and recommendations for the selection and qualification of carbon, low alloys steel and for corrosion resistant alloys (CRAs). One crucial step for the selection of steels for specific sour services application is the determination of stress corrosion cracking regions of environmental severity. By knowing the H<sub>2</sub>S partial pressure and the in-situ pH the region can be determined. The standard provides figures for estimating in situ pH of environments containing H<sub>2</sub>S, CO<sub>2</sub>, bicarbonate ions, and saturated or unsaturated with calcium carbonate. However, the figures provided in the standard do not consider the effect of organic acids such as acetic acid and propionic acid. No details of the reliability of the model presented in the standard have been provided though the Crolet and Bonis model has been referenced in the standard.

#### Papavinasam Model<sup>37, 38</sup>

Papavinasam et al developed an empirical equation based on experiments conducted in an autoclave<sup>37, 38</sup>. The experiments were conducted in at high temperature and high pressure in an autoclave fitted with a commercial pH probe (Omega model PHEH-51S pH probe). The pH probe was connected using a 316SS-3/4" MNPT mounting gland. The autoclave was filled with

7.4 L of test solutions. This amount of solution ensured that the head of the pH probe was immersed, while leaving sufficient headspace at the top of the autoclave for the gases. The pH probe used was chosen because of its ability to operate in an H<sub>2</sub>S environment. Appropriate solution was loaded into the autoclave and was deoxygenated for 24 hours by purging with ultra-high pure (UHP) nitrogen at a rate of 100 mL/min. During all experiments the autoclave motor was set at 200 rpm to stir the solution. Effect of variation of pH on CO<sub>2</sub> and H<sub>2</sub>S partial pressures was determined at 50°C. The autoclave was then continuously pressurized with 10 psi of appropriate gas. The pH was measured after four hours so that the pH variation due to dissolution of gas was overcome and equilibrium was reached. Based on repeat tests, the author concluded that the measure pH values were accurate to 0.3 pH unit.

#### pH in Sweet System

Figure 2 presents the variation of pH with CO<sub>2</sub> partial pressure in distilled water at 50°C. Addition of 4000 ppm HCO<sub>3</sub><sup>-</sup> in distilled water in the form of NaHCO<sub>3</sub> increased and stabilized the pH at 6 (Fig. 3). Similarly increase in pH was observed by the addition of 4,000 ppm of CH<sub>3</sub>COONa in distilled water, which also stabilized the pH at 6. Addition of a mixture of NaHCO<sub>3</sub> and CH<sub>3</sub>COONa, each at 4,000 ppm HCO<sub>3</sub><sup>-</sup> and 4,000 ppm CH<sub>3</sub>COO<sup>-</sup> produced a pH of about 6, indicating the net effect in the presence of two salts. Similar variation of pH as a function of various concentrations of H<sub>2</sub>CO<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> ions are reported in the literature<sup>2</sup>.

On the other hand, the addition of 4000 ppm of CH<sub>3</sub>COOH in distilled water decreased the pH to less than 4. Acetic acid, a weak acid, supplies protons, decreasing the pH further.

In brine solution (Composition in Table 3), the pH observed is almost the same as in distilled water, indicating that the various salts and ions present in the brine have no net effect on pH. As a result, pH depends only on CO<sub>2</sub> partial pressure. Figure 2 also shows the pH for all solutions at 80 psi of CO<sub>2</sub>.

#### pH in Sour System

Figure 2 presents the effect of H<sub>2</sub>S partial pressure on pH. H<sub>2</sub>S partial pressure was varied from 10 to 80 psi. As with the CO<sub>2</sub> solution, the pH decreased with H<sub>2</sub>S partial pressure. Figure 4 shows the results of varying the brine solution on pH in the presence of H<sub>2</sub>S. The addition of 5,000 ppm SO<sub>4</sub><sup>2-</sup> (either as Na<sub>2</sub>SO<sub>4</sub> or as MgSO<sub>4</sub>) had minimal effect on the pH. The same effect has been observed by Miyasaka<sup>35</sup>. (Addition of Na<sub>2</sub>S alone or in the presence of Na<sub>2</sub>SO<sub>4</sub> increased the pH to about 6. In brine solution (Composition in Table 2), the pH observed is almost the same as in distilled water. As a result, pH depends strongly on the H<sub>2</sub>S partial pressure when compared to the variation of the solution species.

#### pH in Combined Sweet-Sour System

Figure 5 presents the effect of temperature on pH in sweet and sour environments in the temperature range between 30°C and 50°C. In both environments, the pH values were at higher temperature higher than those at lower temperature.

Figure 6 presents the pH of the distilled water at a pressure of 80 psi (with 40 psi partial pressures each of H<sub>2</sub>S and CO<sub>2</sub>) and 50°C temperature. Within the experimental error, the results are similar, and the pH remained between pH 4 and 5. The effect of brine concentration on pH in

a 50/50 H<sub>2</sub>S/CO<sub>2</sub> mixed-gas environment using the same salt solutions as in the CO<sub>2</sub> and H<sub>2</sub>S runs. The results obtained were similar to those obtained using individual gases.

Based on the experimentally determined pH and on pH values reported in the literature, the authors developed an empirical equation to predict in situ pH as a function of pCO<sub>2</sub>, pH<sub>2</sub>S, HCO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COOH, and temperature:

The equation can be used only for those two systems that might contain or not bicarbonate from a mineral source like calcite:

1) H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>3</sub>COOH

And

2) H<sub>2</sub>O-CO<sub>2</sub>-H<sub>2</sub>S-CH<sub>3</sub>COOH

$$pH_{final} = -\text{LOG} \left\{ 1.73 \times 10^{-7} \sqrt{[\text{CH}_3\text{COOH}]} + \frac{\left( 5 \times 10^{\left( \frac{P_{H_2S} + P_{CO_2}}{8} \right)^{0.21} + 4.9} + 8.2 \times 10^{-5} [\text{HCO}_3^-] \right)}{\left( 2 \frac{P_{H_2S} + P_{CO_2}}{8} \right)^{0.21} + 9.8} \right\} + 0.006(t - 50) \quad (35)$$

where; [CH<sub>3</sub>COOH] is the concentration of acetic acid in ppm, [HCO<sub>3</sub><sup>-</sup>] is the concentration of bicarbonate ion in ppm, p<sub>H<sub>2</sub>S</sub> is the partial pressure of H<sub>2</sub>S in psi, p<sub>CO<sub>2</sub></sub> is the partial pressure of CO<sub>2</sub> in psi and *t* is the temperature in Celsius.

The Papavinasam's equation predicted reasonably the literature<sup>30,33</sup>. Table 4 compares the pH measured with the computed values. Even if the set of measurements has been taken in a large spectra of temperature 25 to 145°C as well for the pressure of acidic gas P<sub>(CO<sub>2</sub>)</sub>+P<sub>(H<sub>2</sub>S)</sub> where the values vary from 20 psi to 150 psi, the parity graph Figure 7 shows reasonable precision.

### Rodgers Model<sup>39</sup>

W.F. Rodgers developed a simple relation to calculate the pH in aqueous media containing carbonic acid and alkaline constituents<sup>39</sup>. If sufficient alkaline agents are present to convert the carbonic acid to bicarbonates and carbonates the only the latter two ions are present. It is mainly the case in oil well brines which contain calcium and sodium bicarbonates. Thus, the pH can be calculated only by knowing the concentration of carbonic acid and the bicarbonate concentration

(The concentration is expressed in gram-mole/liter).

According to Redger's model:

$$pH = 6.8 + \log(HCO_3^-) - \log(H_2CO_3) \quad (36)$$

In cases where waters contain no alkaline agents are present (absence of sodium and/or calcium bicarbonates). The pH depends only on CO<sub>2</sub>.

$$pH = 4.08 + \log \frac{1}{\sqrt{W_{CO_2}}} \quad (37)$$

Where W<sub>CO<sub>2</sub></sub> is the weight of CO<sub>2</sub> in grams dissolved per liter of water

#### Staples and Holcomb and Cramer Model<sup>40</sup>

Staples et al developed a procedure to predict the pH for solutions at temperatures up to 300°C using H<sub>2</sub>O-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> as model system. They used the extended Debye-Huckel equation for calculating activity coefficients and they pointed out that the selection of good thermodynamic data is critical to predict reliable values of activity coefficients. According to their model: the second dissociation equilibrium constant for sulfuric acid can be determined as follow:

$$K_2^o = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HSO_4^-}} \quad (38)$$

Where a<sub>i</sub> is the activity of the respective ionic species, H<sup>+</sup>, HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. The K<sub>2</sub><sup>o</sup> (the second dissociation equilibrium constant for sulfuric acid) can be related to temperature, according to Hovey and Hepler equation:

$$\ln K_2^o = 199.0185 - \frac{6658.95}{T} - 31.81 \ln T \quad (39)$$

Where T is temperature in Kelvin

The activities of other ions using Debye-Huckel limiting law:

$$\ln \gamma_i = - \frac{z_i^2 S_T I^{1/2}}{1 + A_2 I^{1/2}} \quad (40)$$

Where z<sub>i</sub> is the ionic charge of the species, S<sub>T</sub> is the Debye- Huckel limiting law slope for the activity coefficient at temperature T for a univalent electrolyte, I is the ionic strength; and A<sub>2</sub> is a temperature dependent adjustable parameter defined by:



$$A_2 = 0.78688 + 5.792 \times 10^{-3} t - 3.3027 \times 10^{-8} t^3 \quad (41)$$

where t is temperature in centigrade.

The equilibrium composition of Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solutions at any temperature is obtained by a procedure involving repeated solutions to the general equation, with convergence on the concentration of the ionic species HSO<sub>4</sub><sup>-</sup>. Individual ion activity coefficients are computed at the final ionic strength using the extended Debye and Huckel limiting law.

$$\ln Q_2 = \ln \frac{m_{H^+} m_{SO_4^{2-}}}{m_{HSO_4^-}} = \ln K_2^o + \frac{4S_T I^{1/2}}{1 + A_2 I^{1/2}} = \quad (42)$$

$$199.0185 - \frac{6658.95}{T} - 31.81 \ln T + \frac{4.S_T \left( \sqrt{\frac{1}{2} \sum z_i^2 m_i} \right)}{1 + \left( 0.78688 + 5.792 \times 10^{-3} (T - 273.15) - 3.3027 \times 10^{-8} \left( (T - 273.15)^3 \right) \right) * \left( \sqrt{\frac{1}{2} \sum z_i^2 m_i} \right)}$$

Where Q<sub>2</sub> is the concentration equilibrium constant for the dissociation of the bisulfate ion and m<sub>i</sub> is the molality of the ionic species (H<sup>+</sup>, HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>).

Once H<sup>+</sup> is computed by simultaneously solving Eqns. 38 through 42, pH is computed from this:

$$\text{pH} = -\log(a_{H^+}) \quad (43)$$

This model is a very complex process and has only been demonstrated to H<sub>2</sub>O-Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>. The applicability of this model to sweet and sour environments has not been established.

## DISCUSSIONS

There are several methods by which pH can be estimated including theoretical calculation based on first principle, actual measurements under field operating conditions, and based on combination of laboratory test and computational modeling. Easy methodologies have advantages and disadvantages.

- The theoretical calculation methods are limited by the reliability and accuracy of thermodynamic data including equilibrium constants, heat capacities, and activity coefficients. Substantial differences in the calculated pH can result from the choice of thermodynamic data used in the computations. The solubility of CO<sub>2</sub> reported in the literature also varies considerably.
- Progress has been made in measuring pH at elevated pressures and temperatures, but these techniques are not being widely used. On the other hand, measuring pH at atmospheric pressure after depressurizing does not the pH of the brine solution under pipeline operating conditions due to the loss of acid gases.
- Prediction based on laboratory estimation of pH is only valid if all parameters that would affect in the field are included in the test.

As a result of these variations quantitative determination or prediction of pH neither appears easy. It should further be noted the most estimation is bulk pH which may differ considerably from that at the surface-environment interface where corrosion occurs and surface layers form. For this reason, quantitative measurement of pH may not be required. Qualitative information on pH is however useful to predict corrosion behavior of material. Such qualitative estimation may be made by any of the three methodologies reviewed in this paper as long as the advantages and disadvantages of the methods are recognized before using pH for integrity management purposes.

## SUMMARY

- The theory of pH calculations, methods of determining pH, and models used for predicting pH, and precautions in using pH values for corrosion control have been reviewed highlighting the advantageous and disadvantageous of each methodologies.
- The importance of considering all parameters influencing pH in the estimation of pH has been emphasized. Parameters influencing pH in the oil and gas production environments include concentrations of sulphate, bicarbonate, and acetate ions, the partial pressures of acid gases (CO<sub>2</sub> and H<sub>2</sub>S), buffering species, and temperature.
- It is further pointed out that most pH estimates are only bulk values, and it may not represent the pH at the metal-environment interface where corrosion occurs and surface layers form.

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**Table 1: Ionisation Constants of Acids at 25°C**

Acid	First ionisation constant	Second ionisation constant
Sulphuric	0.79	
Hydrofluoric	3.17	
Formic	3.75	
Acetic	4.75	
Carbonic	6.35	10.25
Hydrogen sulphide	7.00	12.92

**Table 2: Properties of Some Calorimetric pH Sensors**

Sensor	pH range		Color change
	in solution	In entrapped glass	
Methyl orange	3.1 to 4.4	0.0 to 2.0	Red to yellow
Methyl red	4.4 to 6.2	2.5 to 4.6	Red to yellow
Bromocresol purple	5.2 to 6.8	2.0 to 3.1	Yellow to purple
Bromothymol blue	6.2 to 7.6	2.9 to 4.5	Yellow to blue
Phenol red	6.4 to 8.0	2.9 to 4.6	Yellow to red
Cresol red	7.2 to 8.8	4.0 to 5.3	Yellow to red
Phenolphthalein	8.0 to 10.0	11.8 to 14.5	Colorless to pink
Thymolphthalein	9.4 to 10.4	12.0 to 13.0	Colorless to blue
Thymol blue (acidic range)	1.2 to 2.8	0.0 to 1.1	Red to yellow
Thymol blue (basic range)	8.0 to 9.6	4.3 to 5.7	Yellow to blue
Bromothymol blue	6.0 to 7.6	10	

**Table 3: Composition of brine used in Papavinasam Model**

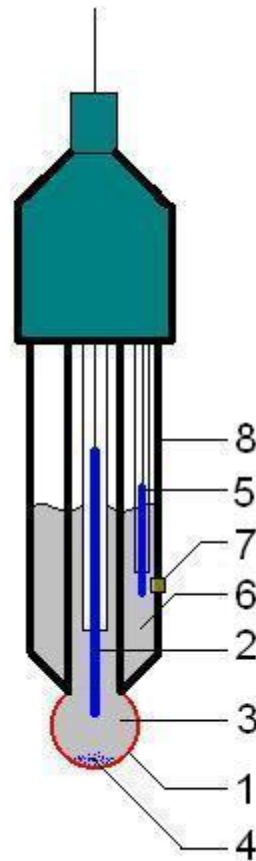
Ion	Ion concentration mg/L
Ca <sup>2+</sup>	2427
Cl <sup>-</sup>	40000
HCO <sub>3</sub> <sup>2-</sup>	1000
K <sup>+</sup>	549
Mg <sup>2+</sup>	529
Na <sup>+</sup>	22394
NH <sub>4</sub> <sup>+</sup>	173
NO <sub>3</sub> <sup>-</sup>	28
S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	29
SO <sub>4</sub> <sup>2-</sup>	704

**Table 4: Comparison between the calculated pH values obtained from the Papavinasam Model with pH measurement taken in this work and in the literature <sup>30,33</sup>.**

$P_{(CO_2)} + P_{(H_2S)}$ (psi)	$[HCO_3]$ (ppm)	t. (°C )	$[CH_3COOH]$ (ppm)	pH (calculated)	pH (measurements*)
116	4274	70	230	5.63	5.70
18.32	1000	25	500	5.08	5.50
33.35	1000	25	500	5.15	5.45
101.5	1000	25	500	5.27	5.40
130.5	1000	25	500	5.29	5.23
152.5	1000	25	500	5.30	5.12
33.35	1000	145	500	5.75	6.60
101.5	1000	145	500	5.87	6.30
130.5	1000	145	500	5.89	5.80
152.5	1000	145	500	5.90	5.70
80	0	50	4000	5.00	4.10 <sup>a</sup>

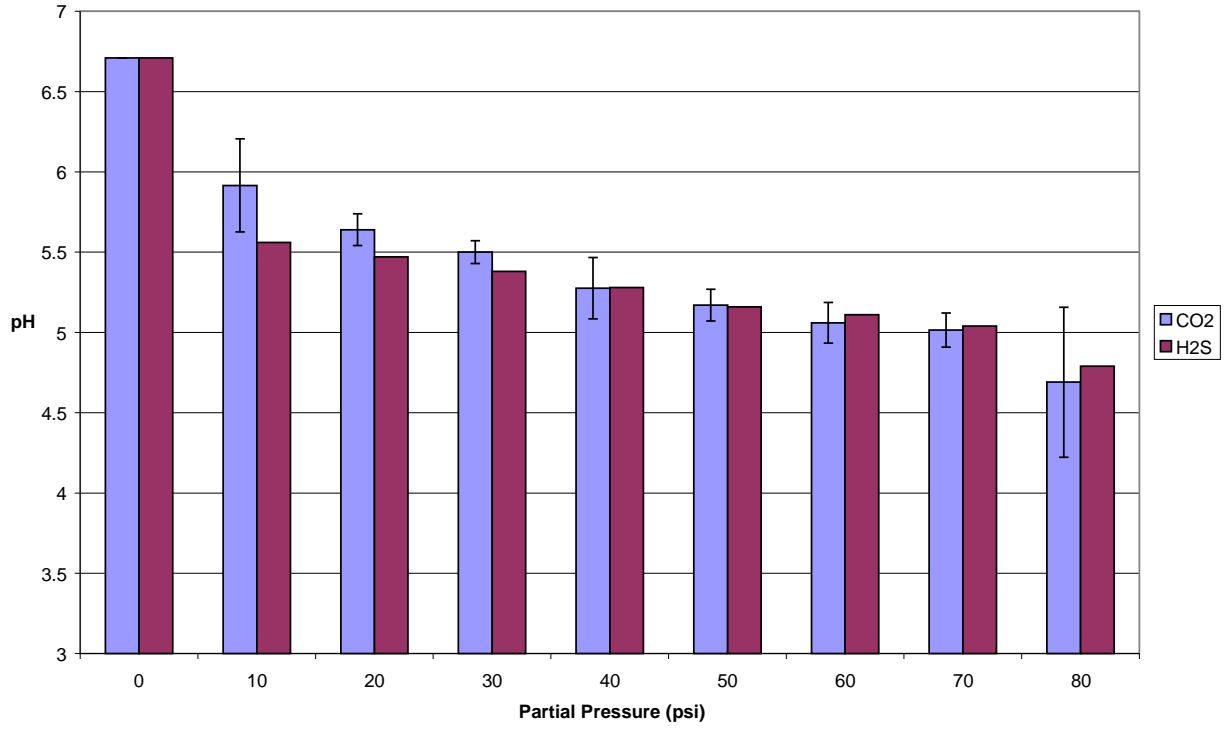
*a: value obtained in this work*

**Fig.1: Schematic Diagram of pH Probe**



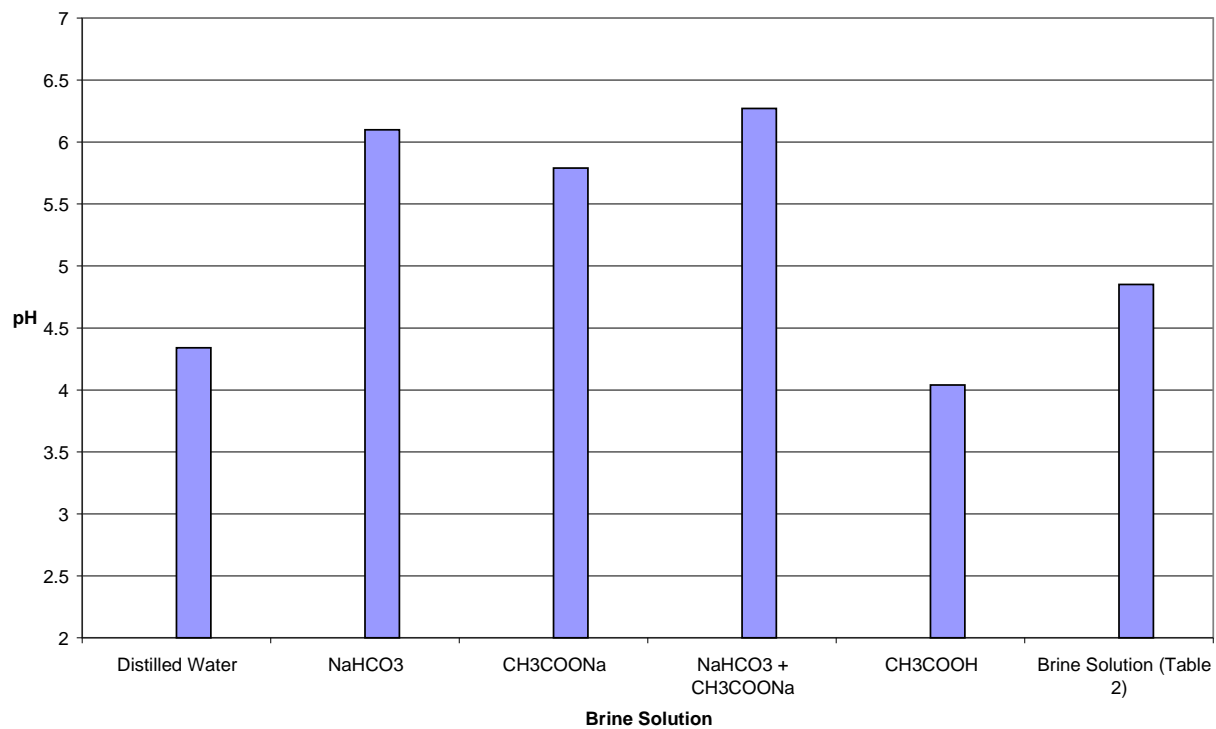
1. Glass blub sensitive to pH; 2. internal electrode (typically silver-silver chloride (Ag-AgCl) or saturated calomel electrode (SCE)); 3. internal solution for electrode; 4. precipitation of silver chloride (when using Ag-Ag as internal electrode); 5. reference electrode (usually same as in 2); 6. internal solution for reference electrode; 7. junction (normally constructed from ceramics, fiber, or asbestos) in contact with solution whose pH is measured; and 8. body (usually constructed from non-conductive glass or plastics) of the electrode.

**Fig. 2: Effects of CO<sub>2</sub> and H<sub>2</sub>S partial pressure on pH in distilled water at 50°C.**

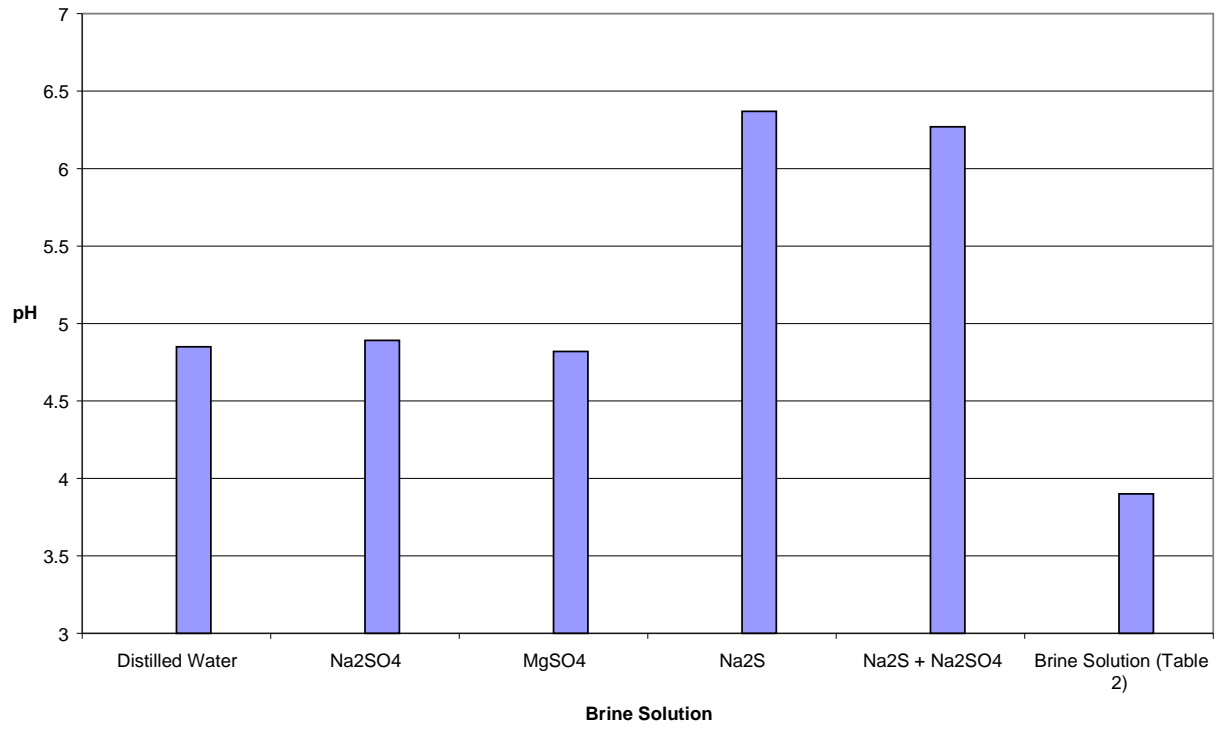




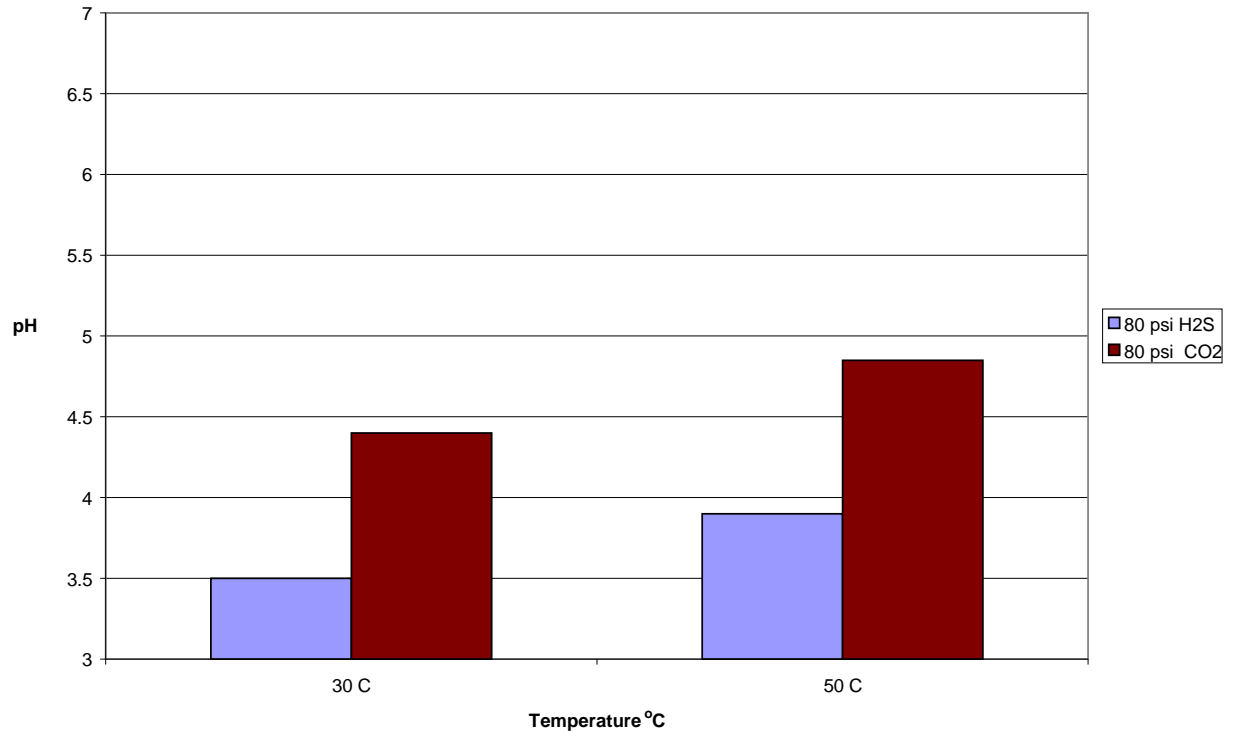
**Fig. 3: Influence of solution species on pH at 80 psi CO<sub>2</sub> partial pressure and at 50°C.**



**Fig. 4: Influence of solution species on pH at 80 psi H<sub>2</sub>S partial pressure and at 50°C**



**Fig. 5: Effect of temperature on pH in brine solution (Table 2).**



**Fig. 6: pH values at 80 psi total pressure in distilled water at 50°C.**

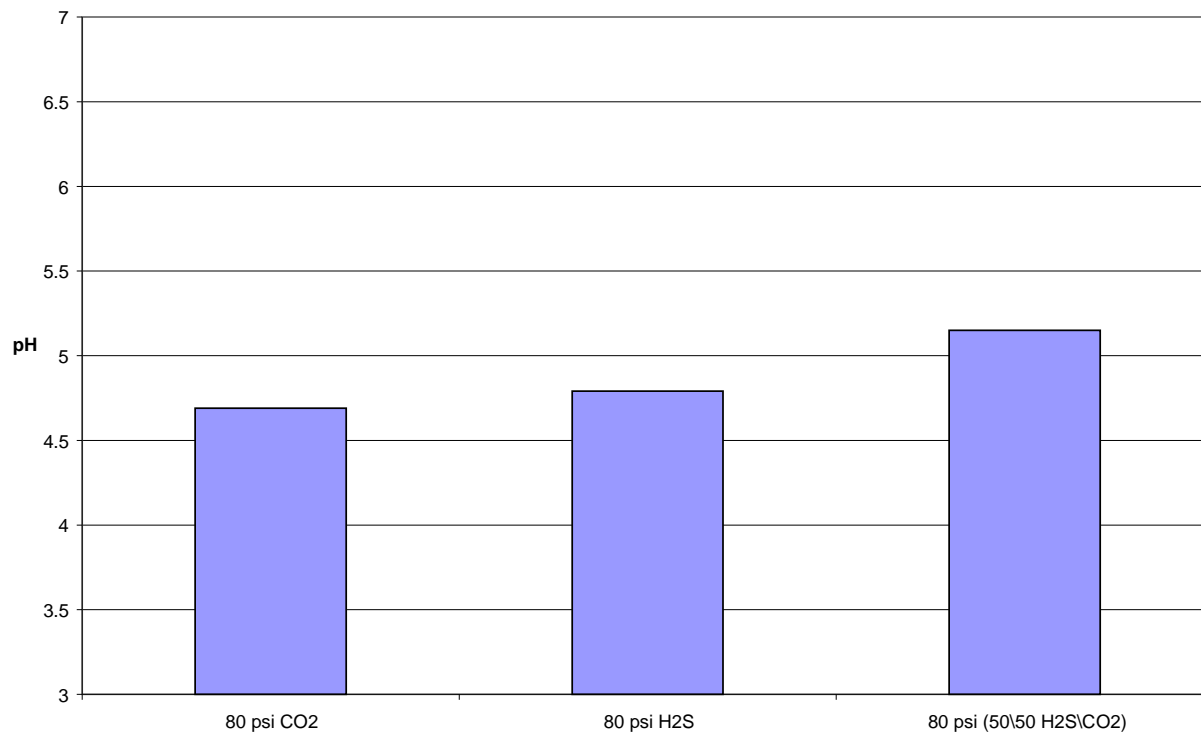


Fig. 7: pH Values from Measurements and from the literature <sup>30,33</sup>.

