

## Understanding Alkalinity for Use in Corrosion Prediction

Bruce Brown  
Institute for Corrosion and Multiphase  
Technology  
Department of Chemical and Biomolecular  
Engineering, Ohio University  
342 W. State St., Athens, OH, 45701  
USA

Yougui Zheng  
Shell Global Solutions  
3333 Highway 6 South  
Houston, TX, 77084  
USA

Jason Dreher  
ChampionX  
11177 S. Stadium Dr  
Sugar Land, TX, 77478  
USA

Marc Singer  
Institute for Corrosion and Multiphase  
Technology  
Department of Chemical and Biomolecular  
Engineering, Ohio University  
342 W. State St., Athens, OH, 45701  
USA

### ABSTRACT

Parameters reported in production fluid water chemistry analyses are used by engineers for determination of scaling tendency and corrosivity, thus promoting optimal production rates while maintaining asset integrity. Water chemistry analysis documents report ion concentrations, total alkalinity, and various graphical data sets related to the tested brine which are designed to assist field engineers. The alkalinity value provided in these documents is of utmost importance to corrosion engineers as it is a measure of the capacity of an aqueous solution to resist changes in acidification. Alkalinity can also be directly linked to the in situ pH of the produced brine and can therefore provide key inputs to assess and predict its corrosivity. Yet, including alkalinity into corrosion production models can be challenging considering there is still much uncertainty among operators about the validity and meaning of the reported alkalinity value. For that reason, recent publications (two AMPP standards) have focused on providing additional guidelines to those who need this knowledge. This is of key importance for the optimization of appropriate and economic corrosion and scaling mitigation strategies. This paper will review the use of the alkalinity term and water chemistry analysis with goals of minimizing confusion and optimizing the use of proper data input for corrosion prediction models.

**Key words:** Alkalinity, water chemistry analysis, solution pH, corrosion prediction

## INTRODUCTION

Historically, a production fluid water chemistry analysis document has mainly been used to indicate possible worst-case scenarios with respect to modeling scale formation. This is because precipitation and growth of sulfate and/or carbonate scales downhole and in a production pipeline diminishes the cross-sectional area of tubing strings, including injection as well as flow lines, restricting the volumetric flow rate of produced oil from a reservoir. These precipitated scales are responsible for many production problems, which can impact the overall life cycle cost of a specific field or wellsite. Results from modeling sulfate and/or carbonate scales are therefore used to indicate the need for scale inhibitors to assist in maintaining a high flow rate of produced fluids. Yet, this same data can be used to predict the in situ pH, and the corrosivity of the multiphase flow in the pipeline, indicating the need for corrosion inhibitors to mitigate corrosion and minimize the probability of failures, which can stop production altogether as well as compromise safety and the environment.

Predictions of scale formation and internal pipeline corrosion by engineers in the oil and gas industry rely on having a good analysis of brine chemistry. Although there is no standard format, all production fluid water chemistry analysis documents provide measured concentrations of cationic and anionic species and a value for alkalinity. The alkalinity value in these documents can be in units of *molar*, *mg/L bicarbonate*, *ppm bicarbonate*, *ppm HCO<sub>3</sub><sup>-</sup>*, and/or *ppm CaCO<sub>3</sub>*. If more than one of these values is given, then they must be equivalent through conversion factors. Chemical analysis documents do vary from company to company but seem to be consistent within the same company over many years. Although most water chemistry documents tend to list organic acids, the values of their concentrations are often left empty, or with ND (*not determined*), because analysis for organic acids was not conducted. This doesn't mean of course no organic acids were present in the brine. Research and publications from Rice University<sup>1,2,3</sup> show the development of an equation and methodology to help identify if organic acids are present in brine samples. Although developed for the industry as an alternative/complementary technique to chemical analysis for the content of organic acids in brines, this methodology is also not routinely conducted. It seems it is not understood that omission of this information can lead to severe misinterpretation of the total alkalinity present in a specimen.

The alkalinity provided in a production fluid water chemistry analysis document is of utmost value to corrosion engineers as it is used as a measure of the acidity of an aqueous solution under operating conditions, but many questions arise about the validity of this value. Total alkalinity of a brine is determined by titration, which is usually reported as bicarbonate (HCO<sub>3</sub><sup>-</sup>) alkalinity. This is because an oilfield reservoir brine is dominated by carbonic species in solution since carbon dioxide is ubiquitous due to the dissolution of carbonate rocks. About 60% of the world's oil reserves are contained in carbonate reservoirs.<sup>4</sup> The definition<sup>5</sup> of electroneutrality for a solution is that "in any single ionic solution, the sum of negative electrical charges on anions must be equal to the sum of positive electrical charges on cations". The alkalinity equation most referenced uses the aqueous concentrations of pH-dependent ions which make up the electroneutrality for an oilfield brine containing numerous cations and anions dissolved from the rock formations of the reservoir. Alkalinity is the sum of the equivalent concentrations of weak acid anions in as far as not compensated by free protons. It is these anions that are available to 'absorb' added protons and thus resist acidification. The pH-dependent species concentrations can be calculated based upon the temperature, pressure, pH, and ionic strength of a brine in simple<sup>6</sup> or complex<sup>7</sup> water chemistry calculations and used in Equation (1):

$$\text{Alkalinity} \left( \frac{\text{mol}}{\text{L}} \right) = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{HS}^-] + 2[\text{S}^{2-}] + [\text{Ac}^-] - [\text{H}^+] \quad (1)$$

Where:

[HCO<sub>3</sub><sup>-</sup>] is the concentration of bicarbonate ions in aqueous solution (mol/L).

[CO<sub>3</sub><sup>2-</sup>] is the concentration of carbonate ions in aqueous solution (mol/L).

[OH<sup>-</sup>] is the concentration of hydroxide ions in aqueous solution (mol/L).

$[HS^-]$  is the concentration of bisulfide ions in aqueous solution (mol/L).

$[S^{2-}]$  is the concentration of sulfide ions in aqueous solution (mol/L).

$[Ac^-]$  is the concentration of acetate ions in aqueous solution (mol/L).

$[H^+]$  is the concentration of hydrogen ions in aqueous solution (mol/L).

Under laboratory conditions where the brine has been sparged to remove  $H_2S$  and there are no organic acids present, the alkalinity determined from a titration will be approximately equal to the bicarbonate concentration,  $[HCO_3^-]$ , in Equation (1), since the other concentrations in the equation are considered negligible. In many water chemistry analyses, the molar concentration of alkalinity determined by an end point titration is converted into a bicarbonate concentration and added to the list of anions. The reason this is done instead of providing the known molar concentration value for alkalinity is confusing to many, including the authors. Since it has always been done this way, recommendations are needed for changes to occur.

One of the main goals of the corrosion engineer is to obtain a “trusted” alkalinity value for each specific production well. This will allow them to use water chemistry analysis to obtain the bulk solution pH at the specific temperature, pressure, and partial pressures of the acid gases along a pipeline to predict general corrosion rates. In situ reservoir pH values are also not available since downhole pH is not of value to the reservoir engineer. Downhole pH is also difficult to measure because of the environmental conditions, so production information and water chemistry analysis are normally used to back calculate the downhole pH of a well.

Field measurements also have variations in the methodology used for collection of the pH measurement. Bulk solution pH measurements for a water chemistry analysis are expected to occur in the field immediately upon collecting a water sample from the well. However, if the well is considered sour, the sample must be transferred to an analytical lab for characterization after sparging with nitrogen to strip the  $H_2S$ . Most water chemistry documents do provide the temperature at which the pH value was collected, which can give the user insight as to whether it was a field or lab measurement, but whether it was a field or lab measurement may not be indicated on a water chemistry document. The recommended practice for field measurements of pH is to use a calibrated pH probe and meter, but the reality is that many people fail to maintain these properly and eventually default to pH paper to consistently get the job done. When reviewing water chemistry documentation, measured pH values such as 6.0, 6.5, & 7.0 may imply that pH paper was used, whereas measured pH values like 6.23, 6.71, & 5.38 would indicate that a pH probe and meter was employed. As a consequence, these reported measured pH values are generally unsuitable for use in a proper quantitative corrosivity assessment.

The overall goal of a corrosion engineer is to show an understanding of the corrosion issues for each specific location and have confidence in mitigation plans which limit corrosion while maintaining acceptable key performance indicators (KPIs) over the lifecycle of an asset. Mitigation of corrosion in a production pipeline can be achieved by addition of inhibitors, the cost of which varies with dosing rates that are based upon mathematical models using the data from water chemistry analyses. The water cut is also expected to increase as the reservoir is depleted, leading to an increased cost to maintain the inhibitor dosing rate. The requirements for validity/accuracy of an alkalinity number for a valid corrosion assessment depend on the case. Generally, when alkalinity is high, not much is to be gained by increasing its accuracy. Conversely, if a high value for alkalinity is unreliable, the corrosion assessment may turn out to be too optimistic. If alkalinity is low, even small errors in it can cause significant errors in corrosion rates, leading to a need for the corrosion engineer to use a conservative estimate and a possibly unrealistically low alkalinity value to ensure a safe assessment of corrosivity. Hence, it is not just the accuracy/reliability of alkalinity that is important but rather the sensitivity of corrosion rates assessed as a function of alkalinity.<sup>8</sup>

Questions from the corrosion community have been increasing about how to properly use the alkalinity and associated concentrations of anions and cations provided in a water chemistry analysis. Using

historical and new publications associated with these issues, the goal of this paper is to provide a review of methodologies being used to clear up possible misunderstandings that may exist for the improvement of reported values in water chemistry analysis in the future.

## DISCUSSION

### The Measurement of Alkalinity

The measurement of alkalinity for a brine using titration with a strong acid indicates the aqueous solution's acid-neutralizing capacity. The measured value is the sum of all titratable bases and may completely incorrect if the wrong end point pH is used.<sup>10</sup>

The measured value of a solution's alkalinity is usually defined by concentrations of carbonate, bicarbonate, acetate, and hydroxide as these species are found in many surface waters and reservoir brines. In theory, the total alkalinity can be calculated from the water composition, but due to inherent inaccuracies, small errors in compositional analysis can lead to larger errors in calculation of alkalinity. Because of this, the value of alkalinity is taken from a proper titration analysis of the field brine.

The quantitative analytical method to measure the concentration of an acid or base in a liquid sample is referred to as acid-base titration. When titrating a basic solution, like brines from oil and gas reservoirs, the typical titrant to use is a strong acid, like HCl. For a carbonate dominant brine, the end point is usually between pH 4.0 and pH 5.0, which fits with the specific use of a bromocresol green indicator. Per ASTM D1067-16<sup>11</sup>, titrations are to be conducted at 25 °C with a pH 4.5 end point. Although the pH 4.5 end point fits with the use of a color indicator, the color titration method was discontinued in 1988 as laboratories moved towards use of calibrated pH meters and probes to plot the titration curve instead of relying on a color change. Both EPA NPDES Method 310.1 and ASTM D3875-15 are summarized in *APPENDIX A: Standards for Titration* and provide titration procedures based on use of an automatic titrator and pH probe/meter combination. Yet, an end point pH of 4.5 will give an incorrect measurement of alkalinity if organic acids are present in the aqueous phase. This is discussed in the next section.

A recent study<sup>12</sup> on determination of alkalinity in oil and gas field brines reviewed the measurement methodologies and the influence of organic acids on alkalinity. Both the Rice titration method<sup>2, 13</sup> and the Henderson-Hasselbalch titration method were reviewed and shown to be derived from the electroneutrality equation. Although this seems like a simple enough process and calculation, there are many misunderstandings and inconsistencies that need to be addressed.

### Titration calculations in the presence of organic acids

For carbonate brines containing organic acids, the end point of a pH measured titration curve becomes less distinct because of the influence of the organic acids. If a default end point of pH 4.5 was used for these types of titrations, the measured alkalinity would be incorrect and lower than the true alkalinity of the brine. Using this lower alkalinity in a water chemistry calculation for a corrosion prediction model will give a lower in situ pH and a higher corrosion rate. Depending upon the environmental conditions modeled in the corrosion prediction, this may lead to higher capital expenditures or higher operating costs related to corrosion mitigation expenses.

A methodology proposed and published by Rice University, as part of the Brine Chemistry Consortium, provided defined oilfield brine collection and preparation procedures for conducting a specific titration using only 10-15 data points from the initial pH down to an end point pH 3.0.<sup>3</sup> This procedure requires the use of a specific gas mixture, 1% CO<sub>2</sub> in N<sub>2</sub> at 25 °C, to sparge the brine for 30 minutes prior to titration, then extended periods of time between additions of titrant to allow sample equilibration, and the use of a specific equation or software to fit the data points. The use of this procedure was shown to provide relatively accurate predictions of organic acid concentration found in the brine without having to conduct IC (ion chromatography) or GC (gas chromatography) analysis methods. This methodology was recently revisited<sup>12</sup> using known brine compositions in a laboratory setting and found to properly account for the effect of organic acids in an acid-base titration. The Rice equation used for this analysis is directly

derived from the electroneutrality equation and can be expressed as follows, with variables described in Table 1:

$$HCl(M) = Alk + \frac{10^{-pH}}{\gamma^{H^+}} - \left[ \frac{fHCO_3^- * K_{1,H_2CO_3} * K_{CO_2} * P_{CO_2(gas)} * \gamma_{CO_2}}{10^{-pH} * \gamma_{HCO_3^-}} + \frac{T_{Ac^-}}{\frac{10^{-pH} * \gamma_{Ac^-}}{f_{Ac^-} * K_{HAc} * \gamma_{HAc,eq}} + 1} + \frac{K_w}{10^{-pH} * \gamma_{OH^-}} \right] \quad (2)$$

Table 1. Table of variables.

Parameter	Description
$Alk$	Total alkalinity (M)
$T_{Ac^-}$	Sum of carboxylate species (M)
$P_{CO_2(gas)}$	CO <sub>2</sub> partial pressure (bar)
$K$	Equilibrium constants
$\gamma$	Activity coefficients
$fHCO_3^-, f_{Ac^-}$	Correction factors (~1)

The simplest form of a titration equation is based on the Henderson-Hasselbalch equation, Equation (3), which is used to define the pH of a solution containing a weak acid (HA) present with its conjugate base (A<sup>-</sup>).

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad (3)$$

Where the generic acid-base dissociation reaction is written as:



The Henderson-Hasselbalch equation can be rewritten in the same form as the Rice equation for comparison (this form referred to as the Henderson equation):

$$HCl(M) = 10^{-pH} + \frac{T_{HCO_3^-}}{\left(\frac{K_{Ca}}{10^{-pH}} + 1\right)} + \frac{T_{Ac^-}}{\left(\frac{K_{HAc}}{10^{-pH}} + 1\right)} \quad (5)$$

The difference between the Henderson (Equation (5)) and the Rice (Equation (2)) approaches is that the Rice methodology requires continuous sparging of the titrant by gaseous CO<sub>2</sub>. Equation (5) works well for modeling titration data collected at atmospheric conditions with bicarbonate and organic acids present (Figure 1). Equation (2) also matches the titration data well although it includes a more pronounced end point for carbonic acid since its procedure includes sparging with CO<sub>2</sub>.

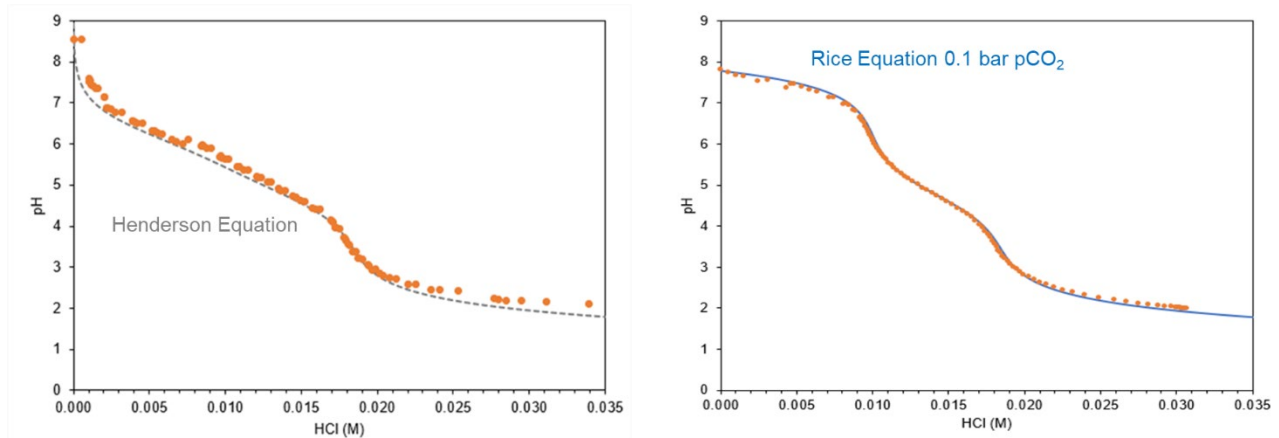


Figure 1. Curve fitting of titration data (dots) with Henderson equation (left) and Rice equation (right). Titration data for 100 ml brine, 0.01 M NaHCO<sub>3</sub> and 0.0085 M CH<sub>3</sub>COONa. Brine for Henderson equation at atmospheric conditions, brine for Rice equation sparged with 0.01 bar CO<sub>2</sub>.<sup>12</sup>

A  $d(pH)/d(mL)$  method originally referred to in a CurTiPot™ (Potentiometric Titration Curves) software<sup>14</sup> uses the derivative of a pH vs. volume titration curve to better define the inflection or equivalence points from titration data instead of using an end point. Because a known concentration of titrant is always used for a titration, a conversion from volume,  $mL$ , to concentration,  $C$ , for the same analysis to use  $d(pH)/d(C)$  is more beneficial in the analysis.<sup>12</sup>

The analysis curves that are fit to the titration data in Figure 1 using Equations (2) and (5) were further analyzed by taking their derivative and plotting in Figure 2 as  $d(pH)/d(C)$  for comparison of the methods. The results of the  $d(pH)/d(C)$  analysis show inflection points for both the added bicarbonate ions and the total alkalinity of the brine sample. The inflection point for the bicarbonate ions is present in both analyses, but the addition of 0.01 bar  $CO_2$  sparge gas vs. atmospheric  $CO_2$  provides a more pronounced peak which can be used in determining the organic acid concentration. The difference in the maxima of these two peaks is caused by the presence of organic acid, which was easily determined under laboratory test conditions (Figure 2, right side).

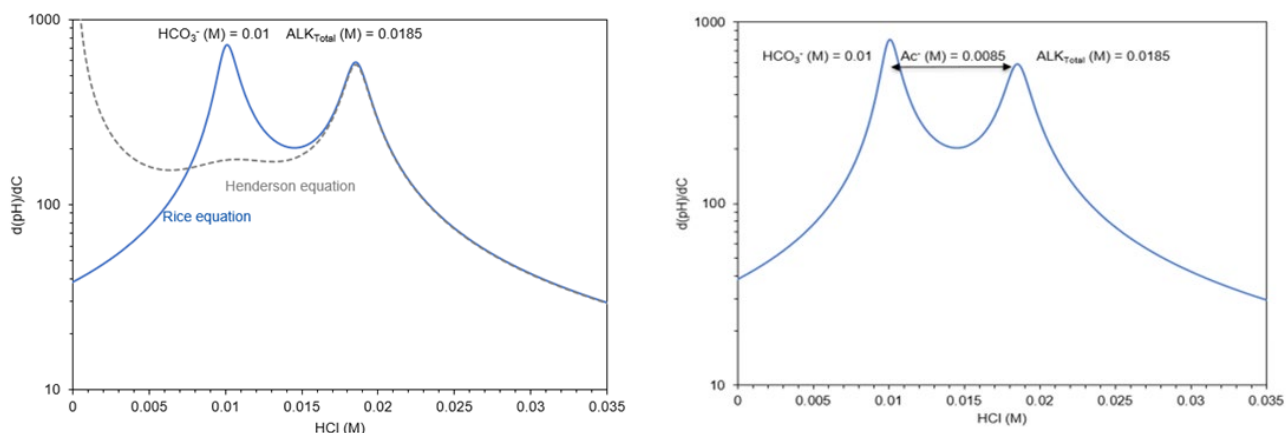


Figure 2. Using the  $d(pH)/d(C)$  analysis to show a comparison of methods and the simple determination of organic acid concentration in a known solution of 0.01 M  $NaHCO_3$ , 0.0085 M  $CH_3COONa$ , without (gray dotted line) and with (blue solid line) 0.01 bar  $CO_2$ .<sup>12</sup>

### Factors that influence pH & alkalinity

How to use the reported pH and the reported alkalinity value in a water analysis should be understood. The reported pH value in a water analysis will have been measured in a depressurized water sample in the field or degassed water sample in the lab. The data given usually lacks reference to a well-defined condition such as the presence of acid gases ( $pCO_2$ ,  $pH_2S$ ). This pH value does not give any direct information related to the in situ reservoir or pipeline bulk solution pH, which is required for corrosion rate prediction. This can lead to mistakes, and result in erroneous decisions, if the sample pH was input for corrosion prediction instead of the in situ pH. Some online probes are available to measure the in situ pH, however, many factors can also influence these measurements, so results need to be validated.<sup>15</sup>

The in situ pH is related to alkalinity but cannot be calculated straightforwardly when the alkalinity is known. The actual pH depends on bulk solution composition details, including the concentration of dissolved acid gases, concentration of ions, total pressure, and temperature. The reverse is also true. Without knowing the detailed water and gas composition, it is not possible to infer the alkalinity from a pH measurement.<sup>15</sup>

Alkalinity is recommended as the input for a corrosion prediction analysis instead of the pH. This is because the alkalinity does not change with temperature, pressure, dissolution or degasification of  $CO_2$

or H<sub>2</sub>S gases, dissolved organic acids, or changes in acid-base equilibria. Acid-base equilibria or dissociation reactions of weak acids, such as H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>S, and CH<sub>3</sub>COOH, have an equal number of moles of hydrogen ions, H<sup>+</sup>, and anions (HCO<sub>3</sub><sup>-</sup>, HS<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>) which are at equilibrium based on the bulk solution pH (see Equation (7) through Equation (12) in the section on Equations for Weak Acids). A list of the environmental factors which can influence pH and alkalinity are shown in Table 2, which corroborates the recommendation for using alkalinity for a corrosion prediction analysis.

**Table 2: List of environmental factors which may influence the pH and alkalinity.**<sup>15</sup>

Which environmental factors influence pH and alkalinity?	pH	Alkalinity
Temperature	Yes	No
Pressure	Yes	No
Dissolution or degasification of CO <sub>2</sub> or H <sub>2</sub> S gas	Yes	No
Dissolved organic acids	Yes	No
Change in acid-base equilibria, e.g., H <sub>2</sub> CO <sub>3</sub> ⇌ H <sup>+</sup> +HCO <sub>3</sub> <sup>-</sup>	Yes	No
Oxidation of the metal	Yes	Yes
Evaporation or condensation of H <sub>2</sub> O	Yes	Yes
Precipitation or dissolution of carbonates	Yes	Yes
Precipitation or dissolution of sulfides	Yes	Yes

In a transmission or production pipeline, the corrosion process itself increases alkalinity by the consumption of protons (unless all Fe<sup>2+</sup> formed precipitates with carbonate). Consequently, the inlet alkalinity of a corroding pipeline is usually lower than its outlet value.

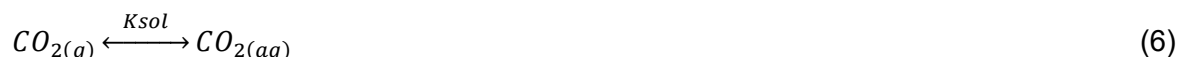
The composition of the brine being produced also changes with time because the aquifer below the hydrocarbons can vary in composition both vertically and laterally in the reservoir. When a brine is being produced, periodic sampling is needed, and multiple samples should be taken.<sup>16</sup>

### Equations for Weak Acids

Carbon dioxide gas is found in all oil and gas reservoirs and is the most dominant gas of the acid gases found for most fields. Hydrogen sulfide, another acid gas, may be present as well. For both gases, there is an equilibrium between the concentrations found in the gas and liquid phases (both aqueous and hydrocarbon).

Once carbon dioxide dissolves in water, a hydration reaction and two dissociations occur with concentrations related to the equilibrium conditions of the system:

Solubility of carbon dioxide in solution:



Hydration of aqueous carbon dioxide:



Dissociation of carbonic acid:



Dissociation of bicarbonate ion:



The hydration of carbon dioxide is considered the slow step in the dissolution process and is defined by a fixed dissociation constant ( $K_{\text{hyd}} = 2.58 \times 10^{-3}$  molar/bar) which gives an approximate ratio of 388 mol  $\text{CO}_{2(\text{aq})}$  for each mol of  $\text{H}_2\text{CO}_3$  in solution. The dissociation constants for carbonic acid and the bicarbonate ion are both functions of temperature and ionic strength. The rate limiting step in the overall reaction is the hydration step in Equation (7) because of the slow kinetics of this reaction.

The reactions and equilibrium constants for these gases require discussion because of the terminology about “bicarbonate concentration” determined by a titration procedure. The bicarbonate species shown forming and dissociating in Equation (8) and Equation (9), respectively, are in solution because of the partial pressure of  $\text{CO}_2$ , Equation (6), so it is not a conserved property because it will change based on the partial pressure of  $\text{CO}_2$ . Because  $\text{CO}_2$  is the dominant acid gas in oil and gas reservoirs, the “bicarbonate” concentration has been used to represent the value of alkalinity, as outlined in Equation (1). This is why the term alkalinity is often misused as bicarbonate. Alkalinity is a conserved value, meaning that it doesn’t change with temperature, pressure, dissolution or degasification of  $\text{CO}_2$  or  $\text{H}_2\text{S}$  gas, dissolved total organic acids, or a change in acid-base equilibria (Table 2). Alkalinity represents the sum of the influence of multiple buffering salts in a solution as shown in Equation (16).

When hydrogen sulfide dissolves in water, two dissociations occur with concentrations related to the equilibrium conditions of the system (as a function of temperature and pH):

Dissociation of aqueous hydrogen sulfide:



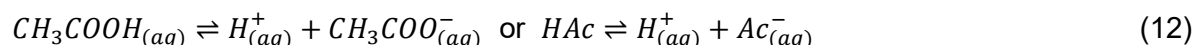
Dissociation of the bisulfide ion:



Hydrogen sulfide is shown here for comparison, but it is assumed that any sample to be used in a titration analysis that may contain  $\text{H}_2\text{S}$  will be sent to a lab and be sparged with  $\text{CO}_2$  to remove any  $\text{H}_2\text{S}$  present before the titration procedure begins.

Organic acids are usually represented in corrosion prediction models by acetic acid,  $\text{CH}_3\text{COOH}$ , since it is usually the most abundant and has a similar  $\text{pK}_a$  (4.8 @ 25°C) to most other organic acids.

Dissociation of Acetic Acid:



To measure the concentration of an organic acid in a brine, analysis methods rely on adding an acid to make acetic acid the dominant species, and then measuring the “total” organic acid concentration as described in the section on Requirements for Water Chemistry Analysis. Only the total organic acid concentrations are known and reported in a water chemistry analysis. This means that consideration for the dissociation of acetic acid must be incorporated into any water chemistry calculations for the pH of the brine under operating conditions to determine the concentration of “free” organic acid available for the corrosion reaction.

The “free” acetic acid,  $\text{CH}_3\text{COOH}$  or  $\text{HAc}$ , is the focus for corrosion rate predictions since, as a weak acid, it will dissociate as needed to provide more hydrogen ions for the reduction reaction, Equation (12). If the mol fractions of acetate,  $[\text{Ac}^-]$ , and free acetic acid,  $[\text{HAc}]$ , are compared during the addition of acid,  $\text{HCl}$  or  $[\text{H}^+]$ , to a solution during titration, the change in concentrations is shown in Figure 3.

In a titration procedure, the brine sample as received usually has a bulk solution at pH 6.8 or higher. If the brine contains acetic acid, then, at pH 6.8, the solution will contain mostly acetate. But, as the titrant (i.e.,  $\text{HCl}$ ) is added to the solution and the pH decreases, the acetate in solution decreases until it is fully



titrated around pH 2.7. This weak acid acts as an additional buffer which requires more  $[H^+]$  to change the overall pH of the brine.

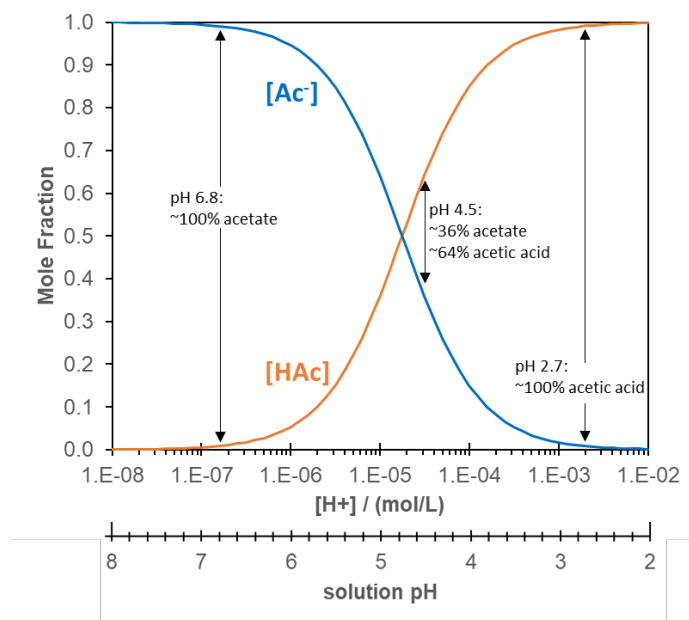


Figure 3: pH dependence of acetate and acetic acid at 25 °C.

The influence of carbonic acid on corrosion was first modeled by de Waard & Milliams<sup>18</sup> in 1975 because it was found in oil and gas reservoirs and the acidity of the brine was highly dependent upon the partial pressure of  $CO_2$ . Since it is a weak acid, it will dissociate as needed to provide more hydrogen ions for the reduction reaction, Equation (14), to maintain the corrosion rate (see “buffering effect” in [19]). The understanding to model weak acids in brines at operating temperatures and pressures of a producing well has been of utmost importance for modeling corrosion and determining mitigation strategies as can be seen by the dates of these two important documents.

Information for engineers to develop a water chemistry program has been provided in the literature for decades. A summary of the available chemical reactions and equilibrium constants was published by Nordsveen, et al.,<sup>6</sup> in 2003, which is used to this day as training documentation for new graduate students and others to the field of corrosion. As with any publication, most of the required information is provided in that document, but some extra calculations and programming effort are required to create a working water chemistry model. This type of model water chemistry model is used to help students and engineers calculate the acidity (or pH) of a brine under a wide range of temperatures and pressures with good accuracy. A new document for AMPP is the Reference Guide TM21476, “A Method for Calculation of Bulk Solution pH Value in Brines Containing Acid Gases and Organic Acids”, which assists any engineer interested in having their own water chemistry model that they can trust to immediately use the methodology provided to develop a spreadsheet or program (APPENDIX B: AMPP Standards / Guidelines).

### Which is the ‘true’ bicarbonate?

The true bicarbonate is the actual  $HCO_3^-$  concentration in equilibrium with a given system and related to temperature, pressure, mol%  $CO_2$ , and ionic strength or activity of the other species in the brine as calculated in Equation (8) and Equation (9). The true bicarbonate concentration is consequently not a conserved variable as it is temperature and pH dependent.

The ‘bicarbonate mg/L’ specified in a water chemistry analysis is given as a representation of the alkalinity value and should be used as such to help determine the bulk solution conditions in the pipeline and at reservoir conditions. The ‘bicarbonate mg/L’ is a conserved variable. In practice, the values of the “true  $HCO_3^-$  concentration” in operating conditions and the “bicarbonate mg/L” (a.k.a. alkalinity) reported in water chemistry report can be very close to each other – this is because most of the alkalinity of an aqueous phase is represented by the  $HCO_3^-$  concentration in pH range commonly encountered in oil and gas production ( $5.5 < \text{pH} < 7$ ). Yet, this is only valid in simple systems that do not contain any other weak acids, such as organic acids, because they too can contribute to alkalinity.

Weak acids can be defined by their generic acid-base dissociation, Equation (4). The three components to this equation are the undissociated part of the acid,  $HA_{free}$ , its anionic conjugate base,  $A^-$ , and the associated cation,  $H^+$ . A weak acid only partially dissociates in the solution. At the equilibrium pH, the concentrations of each of the species can be determined by water chemistry calculations based on the dissociation reactions, equilibrium constants, temperature, and, in some cases, pressure.

Corrosion of carbon steel, such as the internal corrosion of oil and gas pipelines, involves electrochemical and chemical reactions. The chemical reactions are shown above in Equations (7) through (11) and the electrochemical reactions are shown by Equations (13) and (14).

Anodic dissolution of iron:



Cathodic hydrogen reduction reaction:



Using a corrosion prediction model, such as MULTICORP™ †, with the same input conditions (temperature, pressures, type of brine, flow rates), bulk solution pH and initial corrosion rates can be calculated for comparison of the influence of alkalinity on corrosion. In the cases shown in Table 3, the same input conditions for water chemistry and flow regime were chosen for the corrosion prediction model except for alkalinity. Using three different randomly chosen values for alkalinity (high, low, and zero), a direct influence on the acidity of the brine or condensed water can be observed by the change in bulk solution pH, which then is a direct influence on the corrosion rate (Equations (13) and (14)).

Table 3. Influence of alkalinity on predicted corrosion rate

Input Parameters	Higher Alkalinity to Lower Alkalinity			Condensed
Temperature	65 °C	65 °C	65 °C	65 °C
Total Pressure	10 bar	10 bar	10 bar	10 bar
CO <sub>2</sub> content	10 mol%	10 mol%	10 mol%	10 mol%
Brine	3 wt% NaCl	3 wt% NaCl	3 wt% NaCl	-
Superficial gas velocity	2 m/s	2 m/s	2 m/s	2 m/s
Superficial water velocity	1 m/s	1 m/s	1 m/s	1 m/s
Alkalinity (M)	0.02 M	0.005 M	0.0008 M	0.0 M
<b>Output Values</b>				
Bulk solution pH	6.4	5.8	5.0	4.0
Corrosion rate (mm/yr)	2.0	2.7	4.1	8.0

As seen by the output values in Table 3, the main input parameters of temperature, pressure, ionic strength, and flow regime do influence the general corrosion rate prediction, but a valid alkalinity value is required to determine the pH and corrosion rate. These calculations also confirm the sensitivity of the corrosion rates based on the amount of alkalinity as the small change of  $8 \times 10^{-4}$  M from condensed water

† Trade Name

to a lower alkalinity brine dropped the corrosion rate by 50%. Because of this, a corrosion engineer may use a conservative estimate of the alkalinity value to ensure a safe assessment of corrosivity.

A plot of corrosion rate vs. alkalinity in Figure 4 shows sensitivity of between these two parameters for a specific range of alkalinity. For one order of magnitude concentration change at low alkalinity from  $10^{-5}$  M to  $10^{-4}$  M, the corrosion rate decreases by  $\sim 1$  mm/yr. From  $10^{-4}$  M to  $10^{-3}$  M alkalinity, the corrosion rate decreases by  $\sim 2.5$  mm/yr, and from  $10^{-3}$  M to  $10^{-2}$  M alkalinity, the corrosion rate decreases by  $\sim 1.5$  mm/yr. In these conditions with no precipitate forming on the metal surface, the corrosion rate drops by a factor of 3 (7 mm/yr to 2.5 mm/yr) based on the alkalinity change from  $10^{-5}$  M to  $10^{-2}$  M alkalinity.

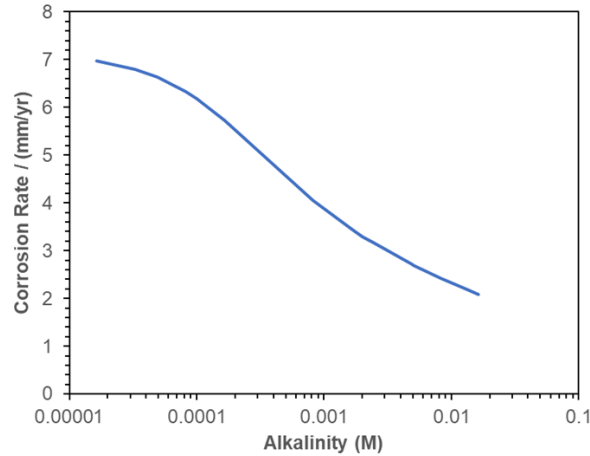
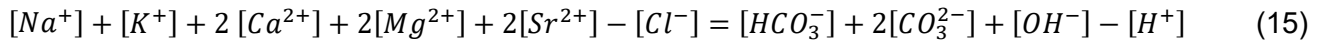


Figure 4. Sensitivity of corrosion rate prediction for different alkalinity brines for operating conditions of  $65^{\circ}\text{C}$ , 10 bar, 10 mol%  $\text{CO}_2$ , 3 wt% NaCl,  $V_{\text{sg}} = 2$  m/s,  $V_{\text{sl}} = 1$  m/s

### Evaluation of Water Chemistry Analysis Information

Using an example electroneutrality equation for a sweet system with no  $\text{H}_2\text{S}$  and no organic acids, the pH-dependent species can be arranged on the right side and the remaining dissolved salt ions on the left side in Equation (15).



With this understanding, alkalinity can also be defined as the difference in total dissolved salt ions (TDS<sup>9</sup>), such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ , etc., which can be considered ‘inert’ in the context of weak acid dissociation, by using Equation (16):

$$\text{Alkalinity} \left( \frac{\text{mol}}{\text{L}} \right) = \sum (c_{\text{inert}} \times z_i) \quad (16)$$

Where:

$c_{\text{inert}}$  is the concentration of inert TDS salt ions (mol/L).

$z_i$  is the valence or charge number of each ion (positive for cations, negative for anions).

One would think that by using the information provided on a water chemistry analysis, the methodology of Equation (16) would also give an appropriate answer for alkalinity (summing up the molar concentrations of cations and subtracting the molar concentrations of anions). This is not normally the case. Although measurements for water analysis of received samples are routinely conducted by skilled analytical chemists, it is not the accuracy of the analysis method which is the problem. Using Equation (16) for data in a water chemistry analysis is not valid for two reasons:

1. The alkalinity may be much smaller than the sum of the positive charges and the sum of the negative charges, limiting the accuracy that can be achieved for alkalinity.

2. The list of ions measured is rarely complete, implying that the (relatively small) value of alkalinity derived is inaccurate.

This type of calculation can easily be tested since a value for alkalinity is provided along with the lists of cation and anion concentrations in a water chemistry analysis and may be helpful in determining the overall cohesiveness of the data provided in the analysis.

When using the cation and anion concentrations in a mechanistic water chemistry model, it is also essential that the electroneutrality equation must be preserved, because a solution cannot have a charge. By rearranging Equation (16) and substituting the given bicarbonate concentration,  $[HCO_3^-]$ , and its valence (-1) for alkalinity, an additional make-up species (cation or anion) must be added to achieve electroneutrality of species in the water chemistry model as shown by Equation (17):

$$\sum(c_{inert} \times z_i) + ([HCO_3^-] \times (-1)) + (make\ up\ ion \times valence) = 0 \quad (17)$$

Because sodium ( $Na^+$ ) and chloride ( $Cl^-$ ) are the most prevalent ions in a water chemistry analysis, they are used for the make-up ion in Equation (17). In other words, if the sum of the first two terms in Equation (17) is positive, then a molar concentration of chloride ions,  $[Cl^-]$ , with a valence of “-1” is added to make the equation true. If the sum of the first two terms in the equation is negative, then a molar concentration of sodium ions,  $[Na^+]$ , is used to make the equation true.

When checking a water chemistry analysis document, if the concentration of inert ions necessary to balance Equation (17) is too “large” (i.e., if the calculated additional concentration is greater than a certain percentage of the given concentration in the water chemistry analysis), it may be assumed that the water analysis is suspect and not usable. The term “large” in this context must be determined by individuals working with the water chemistry analysis documents; the authors have observed additions of these ions from 0.1% to almost 15% of the given concentration to confer electroneutrality but offer no maximum error to avoid. Common reasons for having a “large” discrepancy can be from simple typographical errors to analytical errors, such as overlooking the measurement of barium ions or borate ions which have a strong influence on scaling and pH.

### Requirements for Water Chemistry Analysis

Water chemistry analysis documents all have lists of cations and anions found by chemical analysis and an alkalinity value for calculations with some caveats as described in the Introduction. In reference to the known issues with water chemistry parameters, AMPP Guide 21555<sup>15</sup>, currently under consideration in standards’ committee SC 20 - Internal Corrosion Management, provides a list of guidelines for water chemistry parameters relevant for corrosion prediction. This list of parameters gives recommendations whether these parameters are “*must have for corrosion prediction*”, “*additional data for mechanisms other than CO<sub>2</sub> corrosion*”, and “*data that provides additional insight*” for corrosion. The “*must have*” and “*additional data for mechanisms*” are summarized here:

There are three parameters that are considered “*must have*” in the guide<sup>15</sup>, which are sample location, alkalinity, and organic acid concentration:

- Sample location is necessary as it ties the data reported to the total pressure, partial pressures of acid gases, and temperature found at each location based on production data. The main two locations chosen should be the pipeline inlet and pipeline outlet to provide information needed to develop pressure and temperature profiles along the full pipeline length if one is not provided. The increase in ferrous ions,  $Fe^{2+}$ , from corrosion along the pipeline will influence the bulk solution pH and alkalinity and needs to be considered based on location.
- The alkalinity is the most important “*must have*” parameter which is usually provided in units of mg/L (ppm)  $HCO_3^-$  or mg/L (ppm)  $CaCO_3$ . Remember that this parameter includes more than just the carbonate species and should be determined by a titration procedure. It is also crucial to provide the end point pH of the titration. As mentioned above, the typically used end point pH of

4.5 is not valid if organic acids are present and will yield an incorrect value of alkalinity. However, at least knowing the end point pH used in the titration can enable the user to back calculate the true alkalinity of the aqueous solution.

- The list of organic acid concentrations is also of great importance. Whether the salt name (i.e., acetate) or the acid name (i.e., acetic acid) is mentioned, the concentrations of each organic acid reported in a water chemistry analysis are the total of the salt and acid forms of each specific organic acid. Formates, acetates, propionates, and butyrates are reported when a base (such as NaOH) is added to the water sample to increase the pH and shift the weak acids to their salt form. Formic, acetic, propionic, and butyric acids are reported when an acid (such as HCl) is added to the water sample to decrease the pH and shift the weak acids to their acid form. The  $pK_a$ , or acid dissociation constant, for most organic acids (from acetic to pentanoic) are within the range of 4.75 to 4.95 for temperatures up to 60 °C as reported elsewhere [20]. Because of this, most corrosion prediction models will use the concentrations of these organic acids provided in a water chemistry analysis to calculate the total number of moles of organic acids and convert that to an equivalent ppm concentration of acetic acid as an input parameter. This is a valid input parameter since acetic acid is usually the most abundant organic acid in the list and the most tested in laboratory corrosion studies. It must be recognized that the alkalinity value measured by a titration procedure can be influenced greatly by the organic acid concentration in the brine; a methodology for determining this influence has been defined elsewhere [3] and reviewed in greater detail [12].

Parameters that are considered as “*additional data for mechanisms*”<sup>15</sup> are needed in corrosion prediction. These are pressure & temperature, specific ion concentrations such as  $Ca^{2+}$ ,  $Fe^{2+}$ ,  $Cl^-$ , and  $SO_4^{2-}$ , and total inorganic carbon (TIC).

- The total pressure, partial pressures of acid gases, and temperature at the sample point (as mentioned above) are needed as inputs to the water chemistry program of a corrosion prediction model. The inlet conditions are found in the production rate data.
- The concentrations of dissolved species and organic acids are measured using different laboratory methods. Determination of cation concentrations, such as  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Fe^{2+}$ , and  $Mn^{2+}$ , are done using an ICP (inductively coupled plasma) analysis method or by IC (ion chromatography). Individual organic acid concentrations are determined by IC (ion chromatography) or GC (gas chromatography). Anion concentrations, such as  $Cl^-$ ,  $SO_4^{2-}$ ,  $Br^-$ ,  $CO_3^{2-}$ ,  $NO_3^-$ , and  $PO_4^{3-}$  are best determined by IC (ion chromatography).
- Ion concentrations that are specified for assistance with corrosion issues are mainly focused on having some type of precipitate occur.  $Ca^{2+}$  and  $Fe^{2+}$  concentrations can be used to determine if calcium carbonate or iron carbonate scaling tendencies are much greater than 1. The  $Fe^{2+}$  concentration is also used as an indicator of corrosion, but  $Fe^{2+}$  in the brine sample can be easily oxidized with the ingress of air to form an iron oxide precipitate which changes the sample pH and requires additional analysis for the solids formed. A high  $Cl^-$  content would influence the solubility and activity of species in the brine and the presence of chlorides seems to increase the corrosivity of steel associated with  $H_2S$  corrosion. Sulfate,  $SO_4^{2-}$ , is known to act as a source of sulfur for anaerobic sulfate reducing bacteria which can generate  $H_2S$ , so this is an important ion to consider if microbiologically induced corrosion (MIC) is expected.
- Total inorganic carbon (TIC) concentration may be listed in some analysis, which includes carbonate, bicarbonate, and dissolved carbon dioxide species from the brine sample. To measure the total inorganic carbon, the sample is acidified which drives the equilibria of Equation (6) through Equation (9) to the left to form  $CO_2$  gas, which is then trapped and measured by infrared spectroscopy. This value can be used by entering the concentrations of ions, concentration of total organic acid, and pH of the brine sample at ambient conditions into a water chemistry model, then adjusting the  $CO_2$  gas content until the true bicarbonate concentration of the model is the

same as the total inorganic carbon value. This is a modelled analysis of the brine sample at laboratory conditions assuming that the measured inorganic carbon is approximately equal to the bicarbonate concentration of the degassed sample. The alkalinity value calculated from the model is correct based on Equation (1).

The determination of the total alkalinity value varies widely between different laboratories. It is normally obtained by an acid-base titration procedure but can differ by pH end point and methodology to obtain that value. A more specific procedure and documentation method is necessary for all labs to adopt, to benefit engineers who need to make more informed decisions. A procedure for determining the alkalinity of a brine sample almost immediately after collection in the field was recommended in 2014.<sup>22</sup> This would be considered good practice and a solid basis for going forward because it minimizes or eliminates several potential sources of error.

## Summary

This document reviews issues and concerns faced by the corrosion engineer who needs to obtain a “trusted” alkalinity value. Most issues related to documentation in a water chemistry analysis are based on expecting the corrosion engineer to be familiar with each different companies’ method of presenting analytical data. The following points highlight issues that need attention and understanding by the corrosion community:

- For a carbonate dominant brine containing no organic acids, the end point is usually between pH 4.0 and pH 5.0, some companies choose the end point of pH 4.5, some choose the end point of pH 5.0 for a more conservative alkalinity value.
- The alkalinity value in these documents can be in units of *molar*, *ppm bicarbonate*, *ppm  $HCO_3^-$* , and/or *ppm  $CaCO_3$* . If more than one of these values is given, then they must be equivalent through conversion factors.
- Although most water chemistry documents tend to have labeled spaces provided for concentrations of organic acids, these spaces may be left empty because analysis for organic acids was not conducted. It does not mean no organic acids were present. Blank spaces or spaces with ND (*not determined*) can be found in water chemistry documents which indicate that these tests were not considered but a reason as to why is not usually provided.
- One would think that by using the information provided on a water chemistry analysis, the methodology to sum up the molar concentrations of cations and subtract the molar concentrations of anions should give an appropriate answer for alkalinity. This is not normally the case.
- The true bicarbonate concentration is the one found due to water chemistry calculations and analysis, which shows a specific concentration of  $HCO_3^-$  related to temperature, pressure, mol%  $CO_2$ , and ionic strength or activity of the other species in the brine and is not a conserved value. The ‘bicarbonate mg/L’ value provided in a water chemistry analysis is the alkalinity measured by titration and is a conserved value.

For a water sample with organic acids, alkalinity should not be determined from a titration to pH 4.5. A full titration curve recorded down to pH 3 is recommended. If the full titration curve down to pH 3 is not available, the measured alkalinity should be compensated with a certain amount of total organic acid based on the specific titration end points.

## REFERENCES

1. M. Tomson, A. Kan, G. Fu, X. Wu, "Simultaneous analysis of total alkalinity and organic acid in oilfield brine," Society of Petroleum Engineers, Houston TX, paper no. 93266, (2005).
2. M. Tomson, A. Kan, G. Fu, L. Cong, "Measurement of Total Alkalinity and Carboxylic Acid and Their Relation to Scaling and Corrosion", Society of Petroleum Engineers, Aberdeen Scotland, paper no. 87449, (2006).
3. P. Zhang, S. Huang, N. Zhang, A. Kan, M. Tomson "Automated Analytical Method to Determine Solution Alkalinity of Oilfield Brine in the Presence of Weak Organic Acids" Industrial & Engineering Chemistry Research, vol 58, issue 11, pp 4667-4673, (2019).
4. M. Akbar, B. Vissapragada, A.H. Alghamdi, D. Allen, M. Herron, et al., "A snapshot of carbonate reservoir evaluation,". Oilfield Review, Winter 2000/2001, pp.20–40.
5. Oxford Dictionary of Biochemistry and Molecular Biology (2 ed.), Edited by: R. Cammack, T. Atwood, P. Campbell, H. Parish, A. Smith, F. Vella, and J. Stirling, Publisher: Oxford University Press, Print Publication Date: 2006, Print ISBN-13: 9780198529170, Current Online Version: 2008, DOI:10.1093/acref/9780198529170.001.0001
6. M. Nordsveen, S. Nestic, R. Nyborg, A. Stangeland, "A Mechanistic Model for Carbon Dioxide Corrosion of Mild Steel in the presence of Protective Iron Carbonate Films-Part 1:Theory and Verification," Corrosion Science, vol 59, issue 5, (2003).
7. OLI Studio, OLI Studio 9.6, OLI Systems Inc: Parsippany NJ, (2018).
8. S. Huizinga, personal communication.
9. C. C. Patton, Applied Water Technology, First Edition, Second Printing, Published by Campbell Petroleum Series, Norman, OK, June 1991.
10. Standard Methods Committee of the American Public Health Association, American Water Works Association, and Water Environment Federation. 2320 alkalinity In: Standard Methods For the Examination of Water and Wastewater. Lipps WC, Baxter TE, Braun-Howland E, editors. Washington DC: APHA Press. 1999 DOI: 10.2105/SMWW.2882.023
11. ASTM D1067-16, Standard Test Methods for Acidity or Alkalinity of Water, Annual Book of ASTM Standards, Section 11, Water and Environmental Technology, Volume 11.01, Water (I), DOI: 10.1520/D1067-16
12. J. Dreher, "Developing Methods for Proper Determination of Alkalinity in Oil and Gas Field Brines." Master's thesis, Ohio University, 2022.  
[http://rave.ohiolink.edu/etdc/view?acc\\_num=ohiou1669283750370699](http://rave.ohiolink.edu/etdc/view?acc_num=ohiou1669283750370699)
13. Brine Chemistry Consortium, "Rice BCC Alk-TAc at PCO2.xls", Rice University: Houston Tx, (2000).
14. I. Gebhardt, "CurTiPot – pH and Acid–Base Titration Curves: Analysis and Simulation Freeware", 2007. Available: [http://www.iq.usp.br/gutz/Curtipot\\_.html](http://www.iq.usp.br/gutz/Curtipot_.html)
15. AMPP Guide 21555, Water Analysis for Corrosion Prediction - Sampling Analysis and Interpretation, document under consideration by AMPP Standards Committee (SC) 20, Internal Corrosion Management, September 2022 to present.
16. D. J. Blumer, "Properties of Produced Water," Chap. 10, Vol. 1 - General Engineering, Petroleum Engineering Handbook, L. W. Lake, editor, Society of Petroleum Engineers, 2007.
17. AMPP TM21476, Methods for Calculation of Bulk Solution pH Value in Brines Containing Acid Gases and Organic Acids, document under consideration by AMPP Standards Committee (SC) 14, Oil and Gas - Upstream, November 2022 to present.
18. C. deWaard and D.E. Milliams, "Carbonic Acid Corrosion of Steel", 30 Apr 1975-Corrosion (National Association of Corrosion Engineers)-Volume 31, Issue 5, pp 177-181

19. A. Kahyarian, "Mechanism and Prediction of Mild Steel Corrosion in Aqueous Solutions Containing Carboxylic Acids, Carbon Dioxide, and Hydrogen Sulfide", 2018, Ohio University, Doctoral dissertation. OhioLINK Electronic Theses and Dissertations Center, [http://rave.ohiolink.edu/etdc/view?acc\\_num=ohiou1541154736282768](http://rave.ohiolink.edu/etdc/view?acc_num=ohiou1541154736282768).
20. S. Ayyagari, M. Eslami, B. Brown, and S. Nestic, "Corrosion Mechanisms of Mild Steel in the Presence of Formic Acid and Acetic Acid", AMPP Corrosion/2022, paper #17944
21. J.F. Kopp, "Methods for chemical analysis of water and wastes", Environmental Monitoring and Support Laboratory, Office of R&D, U.S. Environmental Protection Agency, 1983, Method 310.1 & 310.2, EPA Report #600/4-79-020, <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=30000Q10.txt>
22. L. Wang, A.T. Kan, Z. Zhang, F. Yan, Y. Liu, Z. Dai, M.B. Tomson, "Field Method for Determination of Bicarbonate Alkalinity," in SPE International Oilfield Scale Conference and Exhibition, Aberdeen, Scotland, 2014. doi: 10.2118/169758-MS.
23. API RP 45 : Recommended Practice for Analysis of Oilfield Waters.
24. ISO (2003) ISO 5667-3 Water quality - sampling - part 3: Guidance on the preservation and handling of water samples
25. Standard Methods for the Examination of Water and Wastewater 1060-B: Collection and Sampling, url: <https://www.standardmethods.org/action/showTopic?taxonomyUri=part&topicCode=part1000>
26. J.E. Oddo and M.B. Tomson, "Simplified calculation of CaCO<sub>3</sub> saturation at high temperatures and pressures in brine solutions." Journal of Petroleum Technology 34, 07 (1982): pp. 1583-1590.
27. Y.K. Kharaka et al., "SOLMINEQ.88, a computer program for geochemical modeling of water-rock interactions." U.S. Geological Survey Water-Resources Investigations Report 88-4227, 1988.
28. D.A. Palmer and R. Van Eldik, "The chemistry of metal carbonate and carbon dioxide complexes." Chemical Reviews 83, 6 (1983): pp. 651-731.
29. Z. Ma, X. Gao, B. Brown, S. Nestic, and M. Singer, "Improvement to Water Speciation and FeCO<sub>3</sub> Precipitation Kinetics in CO<sub>2</sub> Environments: Updates in NaCl Concentrated Solutions," Industrial & Engineering Chemistry Research 60, 47 (2021): pp. 17026-17035.
30. IUPAC, Chemical Data Series, no. 21, "Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands" (PergamonPress).
31. Personal communication from Dahzhen Xu, Senior Engineer, Petrochina Planning and Engineering Institute – CNPC, November 2022

## APPENDIX A: Standards for Titration

EPA NPDES Method 310.1 The Environmental Protection Agency (EPA) National Pollutant Discharge Elimination System (NPDES) addresses water pollution by regulating sources that discharge pollutants to waters of the United States. This method states that it is applicable to drinking, surface, and saline waters, as well as domestic and industrial wastes for all concentration ranges of alkalinity but recommends avoiding use of titrant volumes greater than 50 mL. Procedures to assist in creating titrants from reagents and procedures for standard titrations or low alkalinity titrations (> 20 mg/L CaCO<sub>3</sub>) using an automatic titrator and pH probe/meter combination to pH 4.5 are provided. Recommendations are given to use 0.02 N titrant for solutions with alkalinity less than 1000 mg CaCO<sub>3</sub>/L or 0.1 N titrant for solutions with alkalinity greater than 1000 mg CaCO<sub>3</sub>/L to increase accuracy in the titration measurement. along with the formulas to use. Equations are provided for calculations, but conversion factors given are not explained in the document.<sup>21</sup>

ASTM D3875-15 (Reapproved 2023) This test method covers the determination of alkalinity in brackish water, seawater, and brines. This is a very detailed standard with procedures which recommend using an automatic titrator and a pH meter for the titration. This standard defines three ions (hydroxide,



carbonate, and bicarbonate) to describe the alkalinity of the water sample. Water samples with pH greater than 8.1 can be defined by all hydroxide (which is a strong acid – strong base titration) or a mixture of all three (which would be a solution containing a strong base and a weak base), or just bicarbonate (if the beginning pH is less than 8.1). The standard recognizes interferences in the measurement are possible by organic materials or anions other than bicarbonate, carbonate, and hydroxide, and caution the user that this procedure does not take anions other than these three into consideration. This method was taken directly from the APWA standard method <sup>21</sup> (or vice-versa), although the APWA standard method is written in much greater detail.

ASTM Standard Test Methods for Acidity or Alkalinity of Water, D1067-16,<sup>11</sup> has the same information as the others mentioned here with similar wording and calculations. This document provides several indicators with their specific pH end point. The color-comparison titration portion of the standard was discontinued in 1988 as there were not enough laboratories interested in participating in the collaborative study required by D2777 practice. This standard covers the determination of acidity or alkalinity of all types of water. This document does not reference ASTM D3875-15 but references the same ASTM documents plus additional ASTM documents D596, D1066, and D1293.

APWA (American Public Works Association) Standard Methods for the Examination of Water and Wastewater, 2320 A. This standard method is the same as D3875-15 but provides greater details about the testing with respect to the use of color indicators. An example is the added information about “phenolphthalein alkalinity,” which is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Bromocresol green or a mixed bromocresol green-methyl red indicator may be used for pH 4.5.<sup>21</sup>

Table 4. Color indicators and their respective colors and pH end points<sup>11</sup>

Indicator	pH range	Color change	pH at end point	Color at end point
Phenolphthalein	pH 8.0 to pH 10	Colorless to red	8.2	Pink
Methyl purple	pH 4.8 to pH 5.5	Purple to green	4.9	Gray-purple
Bromocresol green	pH 4.0 to pH 5.4	Yellow to blue	4.5	Green
Methyl orange	pH 3.2 to pH 4.4	Yellow to red	4.3	Red

## APPENDIX B: AMPP Standards / Guidelines

During the writing of this document, two important documents are under review by AMPP standards committees. Both of these documents were consulted and referenced for this AMPP conference paper. Below are the titles and rationale provided in the draft documents:

### Guide 21555 – Water Analysis for Corrosion Prediction – Sampling Analysis and Interpretation.

Water sample analysis and data interpretation are critical to internal corrosion prediction, especially with respect to CO<sub>2</sub>/H<sub>2</sub>S and organic acid corrosion. Misunderstanding of the water data is a frequent source of error in corrosion prediction. This Guide provides guidelines on using water chemistry data for corrosion prediction, in particular, the issue of how to deal with organic acids and alkalinity including sampling analysis and interpretation.<sup>15</sup>

### TM21476 – Methods for Calculation of Bulk Solution pH Value in Brines Containing Acid Gases and Organic Acids

This standard test method directly provides the methodology to calculate the solution pH for environmental conditions found in the upstream oil and gas industry. A quadratic form of the water chemistry calculation for pH, derived from the electroneutrality equation, was provided for the first version of TM21476 and shown to be equivalent to other calculations which require iterations using a program or solver to achieve the same result.<sup>31</sup> Equation (18) and (19) are used to calculate the bulk pH of solution by using the supporting water chemistry equations provided in Equations (20) through (25). This model

is fully described in the test method, along with the valid parameter ranges. The ease of using this equation in a spreadsheet without a solver can aid corrosion engineers in understanding the impact of temperature, partial pressures, ionic strength, and alkalinity on the acidity of a brine in an upstream oil and gas pipeline environment.

Quadratic form of the water chemistry equation: <sup>17, 31</sup>

$$[H^+] = \frac{-Alk + \sqrt{(Alk)^2 + 4 \times [K_{wa} + (0.0258 \times K_{H_2CO_3} \times HCO_2 \times pCO_2) + (K_{H_2S} \times H_{H_2S} \times pH_2S)]}}{2} \quad (18)$$

Calculation of pH:

$$pH = -\log([H^+]) \quad (19)$$

Henry's constant for solubility of CO<sub>2</sub>: <sup>26</sup>

$$H_{CO_2} = \frac{0.145}{1.00258} 10^{-(2.27 + 5.65 \times 10^{-3} T_f - 8.06 \times 10^{-6} (T_f)^2 + 0.075 I)} \quad (20)$$

Equilibrium constant for solubility of water: <sup>27</sup>

$$K_{wa} = 10^{-(29.3868 - 0.0737549(T_K) + 7.47881 \times 10^{-5} (T_K)^2)} \quad (21)$$

Dissociation constant for carbonic acid: <sup>29</sup>

$$K_{H_2CO_3} = 387.6 \times 10^{-(6.6216 - 1.594 \times 10^{-3} T_f + 8.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} pCO_2 - 0.4772 I^{0.5} + 0.11807 I)} \quad (22)$$

Dissociation constant for aqueous H<sub>2</sub>S: <sup>27</sup>

$$K_{H_2S} = 10^{-(15.345 - 0.045676(T_K) + 5.9666 \times 10^{(-5)}(T_K)^2)} \quad (23)$$

Henry's constant for solubility of H<sub>2</sub>S: <sup>30</sup>

$$H_{H_2S} = 10^{-0.71742672 - 0.012145427(T_C) + 5.6659982 \times 10^{-5} (T_C)^2 - 8.1902716 \times 10^{-8} (T_C)^3} \quad (24)$$

Solution ionic strength:

$$I = \frac{1}{2} \sum c_i \cdot z_i^2 \quad (25)$$

where :

*Alk* = alkalinity in mol/L

*pCO<sub>2</sub>* = partial pressure of CO<sub>2</sub> in bar

*pH<sub>2</sub>S* = partial pressure of H<sub>2</sub>S in bar

*[H<sup>+</sup>]* = molar concentration of hydrogen ions in solution

*T<sub>f</sub>* = temperature in Fahrenheit

*T<sub>c</sub>* = temperature in Celsius

*T<sub>k</sub>* = temperature in Kelvin

*I* = molar ionic strength (M, mol/L).

*c<sub>i</sub>* = the molar concentration of ion *i* (M, mol/L).

*z<sub>i</sub>* = is the charge number of ion *i*.