

Understanding Alkalinity for Use in Corrosion Prediction

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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_3^-* , and/or *ppm CaCO_3* . 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^{1,2,3} 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_3^-) 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.⁴ The definition⁵ 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 simple⁶ or complex⁷ 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:

$[\text{HCO}_3^-]$ is the concentration of bicarbonate ions in aqueous solution (mol/L).

$[\text{CO}_3^{2-}]$ is the concentration of carbonate ions in aqueous solution (mol/L).

$[\text{OH}^-]$ is the concentration of hydroxide ions in aqueous solution (mol/L).



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$[HS^-]$ 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.⁸

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.¹⁰

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 D1067-16¹¹, 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 study¹² 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^{2, 13} 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 3.0.³ This procedure requires the use of a specific gas mixture, 1% CO₂ in N₂ 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 revisited¹² 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:

$$HCl(M) = Alk + \frac{10^{-pH}}{\gamma^{H^+}} - \left[\frac{fHCO_3^- * K_{1,H_2CO_3} * K_{CO_2} * P_{CO_2(gas)} * \gamma_{gCO_2}}{10^{-pH} * \gamma_{HCO_3^-}} + \frac{TAc^-}{\frac{10^{-pH} * \gamma_{Ac^-}}{fAc^- * K_{HAc} * \gamma_{HAc,eq}} + 1} + \frac{K_w}{10^{-pH} * \gamma_{OH^-}} \right] \quad (2)$$

Table 1. Table of variables.

Parameter	Description
Alk	Total alkalinity (M)
TAc^-	Sum of carboxylate species (M)
$P_{CO_2(gas)}$	CO ₂ partial pressure (bar)
K	Equilibrium constants
γ	Activity coefficients
$fHCO_3^-, fAc^-$	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⁻).

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

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 CO₂. 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 CO₂.

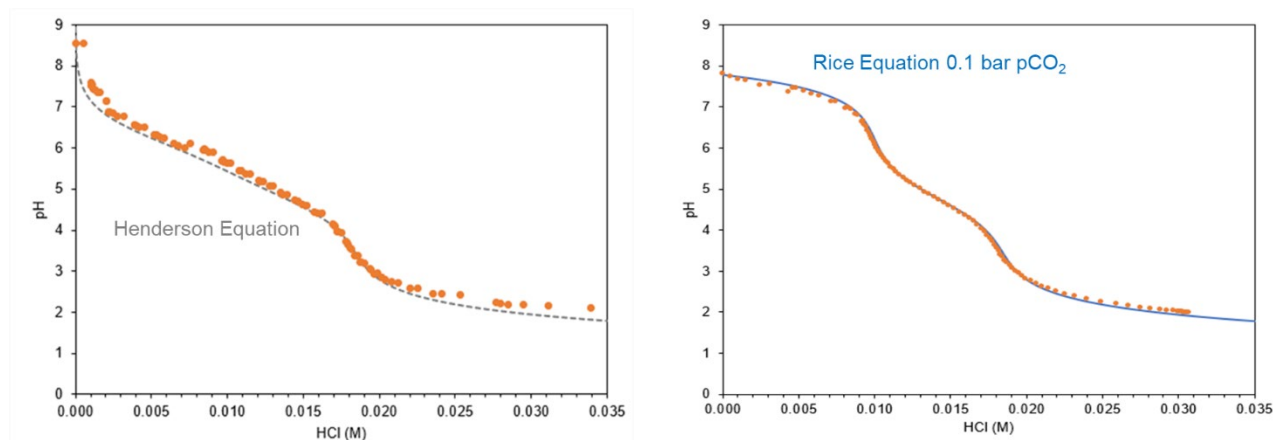


Figure 1. Curve fitting of titration data (dots) with Henderson equation (left) and Rice equation (right).

Titration data for 100 ml brine, 0.01 M NaHCO₃ and 0.0085 M CH₃COONa. Brine for Henderson equation at atmospheric conditions, brine for Rice equation sparged with 0.01 bar CO₂.

A $d(pH)/d(mL)$ method originally referred to in a CurTiPot™ (Potentiometric Titration Curves) software¹⁴ 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.¹²

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).

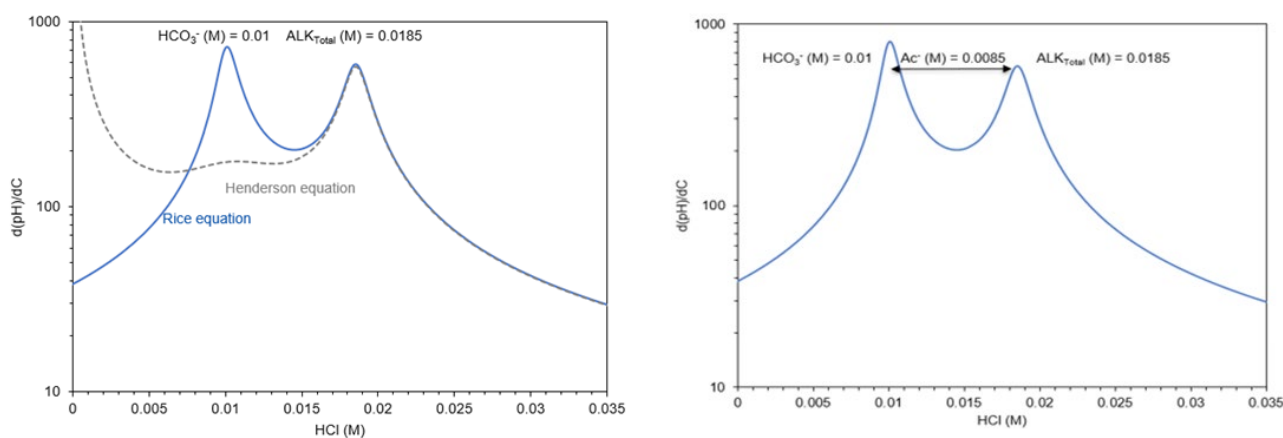


Figure 2. Using the $d(pH)/d(C)$ analysis to show a comparison of methods and the simple determination of organic acid concentration in a known solution of 0.01 M $NaHCO_3$, 0.0085 M CH_3COONa , without (gray dotted line) and with (blue solid line) 0.01 bar CO_2 .¹²

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.¹⁵

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.¹⁵

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