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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-157

Analysis Plan for Determination of pC_{H+} Correction Factors in Brines

Task 1.4.2.2

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1 *Introduction and Objectives*

1.1 Introduction

This Analysis Plan directs the derivation of pH correction factors that will be used to determine the hydrogen ion (H^+) concentration in the high ionic strength brines used in geochemical studies in support of the Waste Isolation Pilot Plant (WIPP). The H^+ concentration is a critical parameter used for calculating geochemical equilibria in electrolyte solutions, especially the high ionic strength brines relative to the WIPP geochemistry model. The H^+ concentration is typically determined via pH measurements in the solutions of interest. However, the measurement of pH in high ionic strength solutions using standard National Bureau of Standards (NBS) operational methods (Bates, 1973) does not provide an accurate measure of the H^+ concentration due to a number of factors (see discussions in Knauss et al., 1990; and Rai et al., 1995). The most significant factor of concern for WIPP studies are the potentially large liquid-junction potentials and the formation of species such as HSO_4^- and $H_2B_4O_7$ that can consume H^+ during electrode standardization (Rai et al., 1995).

In the commonly used combination pH electrodes, the liquid-junction potential arises from differences in ionic diffusivity between the reference electrode solution (typically 3 M KCl) and the sample solution. The measurement of pH using combination electrodes assumes that the liquid-junction potential of the cell in the electrode remains constant between the pH standardization buffer solutions and the samples to be measured. This assumption is valid as long as the ionic strength of the unknown solutions are not significantly higher than the standard buffer solutions (i.e. <0.1 m). However, in higher ionic strength brines pH measurement with a combination electrode is affected because the liquid-junction potential can no longer be assumed as constant between the standard buffer solutions and the samples.

Due to these difficulties it is necessary to correct the measured pH values in brines in order to gain an accurate measure of the hydrogen ion concentration (pC_{H+}). Rai et al. (1995) proposed a relatively simple procedure for estimating pC_{H+} in concentrated brines using commercially available combination glass electrodes. They showed that this procedure gave reliable results (± 0.05 pC_{H+}) units over a wide range of ionic strengths and pC_{H+} values. Rai et al. (1995) show that the H^+ concentration in unknown samples of a given electrolyte (e.g. NaCl) at a fixed molarity can be estimated using the following relation:

$$pC_{H+} = pH_{obs} + A \tag{1}$$

where pH_{obs} is the measured pH reading of the unknown sample with a calibrated combination glass electrode, and A is defined as:

$$A = \log \gamma_{H+} + (F/2.303RT)\Delta E_j \tag{2}$$

where γ_{H+} is the molarity-scale activity coefficient of H^+, and ΔE_j is the difference in liquid-junction potential between the standards and solutions. Although neither term on the right-hand side of Eq. (2) can be independently measured, the combination of the two is measurable. Thus, the constant A can be obtained empirically through a modified Gran titration.

1.2 Objectives

The objective of this AP is to derive the pC_{H+} correction factors (A) for a broad range of WIPP-relevant brines. These brines include simple single electrolyte brines (e.g. NaCl, Na_2SO_4, or $MgCl_2$), two electrolyte brines (e.g. NaCl + $MgCl_2$), simplified multi-component brines, and full-strength WIPP brines (GWB and ERDA-6). The AP will also address whether the same correction factors (A) can be used for combination glass electrodes from different manufacturers or if each brand of electrode requires a unique value for A. Finally, the correction factors derived in this study will be compared to other correction factors in the published literature.
Once the correction factors are determined they will be used to calculate the pC_{H+} in experimental solutions based on observed pH readings. These pC_{H+} values can then be used in other analyses to derive thermodynamic properties needed for WIPP geochemical modeling. Therefore, this study is considered a compliance decision analysis.

2 Approach

2.1 General Procedure

The purpose of this AP is not to provide a detailed discussion of the methods used to generate the data required for derivation of the pC_{H+} correction factors. However, a brief description of the method is provided here for reference. The experimental data used in this AP is collected under Test Plans TP 06-02, *Iron and Lead Corrosion in WIPP-Relevant Conditions* (Wall and Enos, 2006) and TP 10-01, *Experimental Study of Thermodynamic Parameters of Borate in WIPP Relevant Brines at Sandia National Laboratories Carlsbad Facility* (Xiong, 2010).

The modified Gran titration method involves titrating stock electrolyte solutions of known concentration with standard solutions of HCl or NaOH and recording the changes in measured pH as a function of the amount of titrant (HCl or NaOH) added. All stock solutions are prepared with DI water and reagent grade salts. Titrant solutions are either commercially purchased solutions or carefully prepared in the laboratory and then standardized using accepted methods. All solution preparations are recorded in a scientific notebook. Table 1 lists the stock solutions and titrants used for this analysis.

Table 1. Solutions Used in Titrations

Solution	Titrant	
	HCl	NaOH
0.1 m to 5.14 m NaCl	0.01 M; 0.1 M; 1.0 M	--
0.1 m to 1.0 m Na_2SO_4	0.1 M	--
0.01 m to 2.0 m $MgCl_2$	0.01 M; 0.1 M	--
mixed NaCl - $MgCl_2$	0.01 M	--
mixed NaCl - Na_2SO_4	0.1 M	--
Simplified ERDA-6	0.01 M	--
Simplified GWB	0.01 M	1.0 M
ERDA-6	1.0 M	1.0 M
GWB	1.0 M	--

Once the stock solutions have been prepared the modified Gran titration can be conducted either by hand or using an auto titrator (both methods have been used in this exercise). The titration proceeds by adding a known amount of electrolyte solution to a titration vessel and then adding a known amount of titrant to the solution. A fresh aliquot of titrant (acid or base) is added to the titration vessel when the measured pH stabilizes to within 0.05 pH units. After each addition of titrant, the stabilized pH value and the incremental and total volume of titrant added are recorded. These data are then recorded in the scientific notebook.

2.2 Data Analysis

Rewriting Eq. (1) as a logarithmic expression yields:

$$- \log (C_{H+}) = - \log (H^{+}_{obs}) + A \tag{3}$$

Rearranging Eq. (3) and taking the antilog of the result gives the equation:

$$H^{+}_{obs} = 10^{A} C_{H+} \tag{4}$$

The pC_{H+} correction factor, A, can then be obtained from the Gran titration data by plotting the moles of added free H^+ per liter ($H^{+}_{free,add}$) against the H^{+}_{obs} (i.e., 10^{-pHobs}). The logarithm of the slope of this curve is the correction factor A needed to convert the measured pH reading to pC_{H+}.

It is important to note that the moles of added free H^+ per liter must be calculated from the titration data. In addition, the method of calculation will differ depending on the particular electrolytes that are present in the brine of interest. The details for the calculation of $H^{+}_{free,add}$ are discussed below for each of the major electrolytes used in this study.

NaCl Brines – In brines containing only NaCl there are no other species (such as HSO_4^- or $H_2B_4O_7$) that can consume added H^+ during an acid titration. Thus, the amount of acid added during titration should correspond to the free H^+ added ($H^{+}_{free,add}$). The free H^+ added in moles per liter can then be determined with the following formula:

$$H^{+}{}_{free,add} = \frac{V_{add} N}{V_i + V_{add}} \tag{5}$$

where V_i is the volume of brine added to the titration vessel (ml), V_{add} is the volume of standardized acid addition (ml), and N is the normality of the standardized HCl solution.

A plot of H^{+}_{obs} versus $H^{+}_{free,add}$ should result in a linear trend. However, the presence of small amounts of impurities such as soluble bicarbonate may consume minor amounts of H^+ at the beginning of a titration resulting in non-linear behavior at low values of $H^{+}_{free,add}$. These portions of the plots should not be used in determining the slope of the data trend.

Borate Brines – As with sulfate brines, the addition of acid to brines containing borate will result in significant consumption of added H^+ due to the formation of $H_2B_4O_7$. Here again the consumption of added HCl by borate complexes must be accounted for when calculating

$H^+_{free,add}$. Because the formation of borate species is rather complex the "K_{app}" method used for sulfate brines is not practical and an empirical approach is used. In this case the equivalence point for $H_2B_4O_7$ formation must be determined in a separate titration using the same volume of brine and standardized acid concentration as will be used in the Gran titration. From this equivalence point determination the volume of acid required to reach the equivalence point is used to calculate $H^+_{free,add}$ as follows:

$$H^+_{free,add} = \frac{(V_{add} - V_{eq})N}{V_i + V_{add}} \tag{6}$$

where V_{eq} is the volume (ml) of acid added to reach the equivalence point and all other variables are as defined for Eq. (5).

Na_2SO_4 Brines – In brines containing Na_2SO_4 the addition of HCl results in the formation of bisulfate ions (HSO_4^-). The concentration of HSO_4^- that is formed is dependent on the total sulfate concentration of the brine and the amount of acid added. As long as the amount of added acid is small, the formation of HSO_4^- will not significantly alter the total sulfate concentration of the brine and the A factor will remain constant throughout the titration. However, bisulfate formation can consume a significant quantity of added HCl and it becomes necessary to account for bisulfate formation when determining the correct value of $H^+_{free,add}$. In this case the amount of free H^+ added to solution is calculated using the equation:

$$H^+_{free,add} = \frac{H^+_{add}}{1 + K_{app}[SO_4^{2-}]} \tag{7}$$

where H^+_{add} is calculated according to Eq. (5) for borate-free brines or Eq. (6) for borate-containing brines, $[SO_4^-]$ is the molar sulfate concentration of the brine and K_{app} is the apparent molar equilibrium constant for the bisulfate formation reaction:

$$H^+ + SO_4^{2-} = HSO_4^- \tag{8}$$

K_{app} is determined for the Na_2SO_4 concentration of interest using the Pitzer thermodynamic model. The method used to calculate K_{app} is discussed in Section 2.3.

NaOH Titrations – Rai et al. (1995) showed that the correction factor A can also be determined using modified Gran titrations with NaOH as the titrant. When NaOH is used as a titrant a different formulation must be used to calculate $H^+_{free,add}$ that accounts for the dissociation of water. The amount of NaOH added during the titration is converted to $H^+_{free,add}$ through the equation:

$$H^+_{free,add} = \frac{K_W}{OH^-_{add}} \tag{9}$$

where K_w is concentration-dependent dissociation constant of water and OH^-_{add} is determined by:

$$OH^-_{add} = \frac{V_{add} N}{V_i + V_{add}} \tag{10}$$

where V_i is the volume of brine added to the titration vessel (ml), V_{add} is the volume of standardized base addition (ml), and N is the normality of the standardized NaOH solution. K_w is determined for the brine concentration of interest using the Pitzer thermodynamic model. The method used to calculate K_w is discussed in Section 2.3.

It should be noted that the presence of OH^- consuming species in brines for which A is to be determined using base titrations will require special consideration similar to sulfate and borate for acid titrations. For WIPP-relevant brines (especially GWB) the presence of significant quantities of magnesium will result in precipitation of $Mg(OH)_2$, which must be accounted for if base titrations are used.

2.3 Calculation of Equilibrium Constants

The determination of $H^+_{free,add}$ for acid titrations in brines containing sulfate and for all titrations using NaOH requires the calculation of appropriate equilibrium constants. This includes the equilibrium constant for bisulfate formation via the reaction given in Eq. (8) and the dissociation constant of water, both of which are dependent on the composition of the brine. The Pitzer thermodynamic model is used to calculate these constants for each brine of interest with the EQ3/6 geochemical modeling program. The bulk composition of each brine is input into EQ3, which then calculates the equilibrium distribution of the various chemical species in the brine. The needed equilibrium constants are then calculated from the results using the following relations for bisulfate formation and water dissociation, respectively:

$$K_{app} = \frac{[HSO_4^-]}{[H^+][SO_4^{2-}]} \tag{11}$$

$$K_W = [H^+][OH^-] \tag{12}$$

where the values in brackets are the molar concentrations of the indicated species.

3 Tasks

There are four tasks associated with this AP. The primary analyst for this AP is Gregory Roselle. Assistance with data assembly and screening will be provided by Leslie Kirkes. All tasks associated with this AP should be completed by June 30, 2011.

3.1 Task 1 – Data Assembly and Screening

Numerous analysts within the geochemistry group have conducted modified Gran titrations on various brines of interest and using differing combination electrodes. Task 1 involves

identifying and gathering all of this data into a coherent package. As part of this exercise all of the scientific notebooks that contain the titration data will be reviewed and the data will be verified against notebook entries. Data that cannot be verified (either the titration data or solution preparation) will be screened out of this analysis.

3.2 Task 2 – Calculation of K_{app} and K_w

Those titration data sets that require K_{app} or K_w for further analysis will be identified. EQ3 runs will be initiated for the compositions relevant to those titration data and the results will be used to calculate the necessary equilibrium constant. Calculation of the equilibrium constants will be documented in an Excel spreadsheet.

3.3 Task 3 – Determination of Correction Factors

For each titration data set, the appropriate methods outlined in Section 2 will be used to determine the pC_{H+} correction factor A. Once correction factors have been calculated for all of the titration data, the data will be analyzed to see if a generalized equation can be formulated to calculate the value of A as a function of brine composition.

3.4 Task 4 – Application of Results

Once the data analysis is completed an Analysis Report will be issued that summarizes all of the results. These results will also be used to formulate a unified procedure for determining pC_{H+} from observed pH values. This procedure will be implemented either through a revision of SP 12-14, *Use of pH Meters and Electrodes*, or by issuing a new SP.

4 Software List

The following computer code will be used for different tasks associated with this Analysis Plan:

- EQ3/6 version 8.0a (qualified under NP 19-1 for execution on platforms with Microsoft Windows 95, 98, 2000, NT4, XP, Vista, and Window 7).

Commercial off-the-shelf spreadsheet programs, such as Excel, may also be used for data manipulation and plotting.

5 Special Considerations

No special considerations have been identified.

6 Applicable Procedures

All applicable WIPP quality-assurance procedures will be followed when conducting these analyses. Training of personnel will be done in accordance with the requirements of NP 2-1, *Qualification and Training*. Analyses will be performed and documented in accordance with the requirements of NP 9-1, *Analyses* and NP 20-2, *Scientific Notebooks*. All software used will meet the requirements of NP 19-1, *Software Requirements* and NP 9-1, as applicable. The analyses will be reviewed following NP 6-1, *Document Review Process*. All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

7 References

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