SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

Analysis Report for Determination of pH Correction Factors for Brines under AP-157 Rev.1

Effective Date: 09-20-2021

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WIPP:4.4.2.2.1:TD:QA-L:RECERT:556532

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1 Introduction and Objectives

This Analysis Report (AR) documents the determination of pH correction factors for the observed pH readings. The correction factor converts the observed pH reading recorded from the brines used in geochemical studies in support of the Waste Isolation Pilot Plant (WIPP) to a corrected pH value. The data analysis in this AR falls under AP-157 Rev.1 *Analysis Plan for Determination of pH Correction Factors in Brines* (Kirkes et al, 2021). Measurement of pH in some solutions can be challenging due to numerous factors such as high ionic strength, elevated or lowered temperature, complex matrix composition, etc. (Knauss et al., 1990; and Rai et al., 1995). The measured pH can be corrected by applying the correction factor, empirically obtained from a specific test solution.

The correction factors were determined for various brines and solutions, using a modified Gran titration technique, as described in SP 12-14 Rev.5 *Use of pH Meters and Electrodes* and using equations described below and in AP-157 Rev.1 (Kirkes et al, 2021). The corrected pH, pcH or pmH can be determined using Equation 1 (Rai et al., 1995):

$$pcH\ (or\ pmH) = pH_{obs} + A \qquad \textbf{Equation 1}$$

where:

pcH -negative base 10 logarithm of Molarity of H^+

pmH -negative base 10 logarithm of molality of H^+

pH_{obs} -the observed pH reading of the sample

A -a unitless value that is **the correction factor** that is directly added to the in-situ observed pH reading (Roselle, 2011).

Equation 2 shows the variables needed to calculate A.

$$A = log\,\gamma_{H^+} + \left(\frac{F}{2.303RT}\right)\Delta E_j \qquad \textbf{Equation 2}$$

where:

A -correction factor

γ_{H^+} -a unitless Molarity- or molality-scale activity coefficient of H^+

F -the Faraday constant (C/mol, coulombs per mole)

R -the ideal gas constant (8.314 $mol^{-1}\cdot K^{-1}$)

T -Temperature in Kelvin

ΔE_j -the Difference in liquid-junction potential between the standard and solutions, in Volts (V)

Terms on the right-hand side of equation (2) can not be measured independently and therefore obtained directly using a modified Gran titration as per SP 12-14 Rev.5 (Kirkes, 2018). The pH

A was determined by plotting the observed concentration of H^+ , i.e., $[H^+] = 10^{-pHobs}$ (M or m) observed vs. the added H^+ , i.e., $[H^+]$ (M or m), which is the modified Gran titration plot and then calculating the base 10 logarithm of the slope of the line (Roselle, 2011; Rai et al., 1995).

This AR focused on calculating the correction factors for Task 2 and Task 6 outlined in Test Plan (TP) TP 18-01 Rev.1 (Kirkes, 2020a). All data analyzed in this AR was documented in the First Milestone Report for TP 18-01 (Kirkes, 2020b). This AR contains a compilation of the current titration results and comparison of experimental data to literature data and previous experimental data collected under the WIPP program.

2 Materials and Methods

2.1 Scope

The scope is to analyze the data collected under Task 2 and Task 6 from the task list listed in Table 1. Data for these tasks, were documented in the First Milestone report for TP 18-01 (Kirkes, 2020b). Data analyzed in this report were compared with relevant studies from the literature.

Table 1. Task List from TP 18-01 Rev.1

Task #	Task Description
Task 1	*pH correction factor determination for $MgCl_2$ brines ranging in concentrations from 1 M-3 M at temperatures from 25-90 °C.*
Task 2	*pH correction factor determination for NaCl brines ranging in concentrations from 1 M-5 M at temperatures from 25-90 °C.*
Task 3	*pH correction factor determination for Na_2SO_4 brines ranging in concentrations from 0.1 M-2 M at temperatures from 25-90 °C.*
Task 4	*pH correction factor determination for WIPP relevant brines containing organics (Oxalate, Acetate, Citrate, EDTA) at temperatures from 25-90 °C.*
Task 5	*pH correction factor determination for WIPP brines containing borate at temperatures from 25-90 °C.*
Task 6	*pH correction factor determination for WIPP relevant brines (e.g. GWB, ERDA-6, SGWB) at temperatures from 25-90 °C.*

Note: SGWB stands for Simplified GWB and is defined in Table 13 of this AR.

2.2 Instrumentation

Table 2 shows instruments used for collection of the data analyzed in this report.

Table 2. A list of instruments

Instrument	Model/Description

Titrator-1	Mettler Toledo- G10S
Titrator-2	Orion Research-EA940/960
pH electrode-1	Mettler Toledo DGi-115SC-combined glass pH electrode with a fixed ground-glass sleeve junction. Temp (0-100 °C)
pH electrode-2	ThermoFisher Scientific-Ross sure flow semi-micro electrode. 8175BNWP. Epoxy housing, with sure-flow junction. Temp (0-100 °C)
pH electrode-3	Mettler Toledo DGi-101SC-combined micro-glass pH electrode. Ceramic frit junction. ARGENTHAL™ reference system. Temp (0-100 °C)
ICP-AES	Perkin Elmer- Optima 8300 and ESI autosampler Model SC-2D.
IC	Thermo Scientific Dionex ICS-6000 outfitted with a AS23 4 mm column and AG23 4 mm guard column.
Thermometer-1	Electro-therm Model TRH670A. Temp. (-40 to 150 °C)
Thermometer-2	Ertco-Eutechnics Model 4400. Temp. (0-120 °C)

Note: All relevant SPs and their current revisions were used to collect data for this AR.

2.3 Solution Preparation

All solutions were prepared on a molal basis (i.e. molality in mol/kg-H_2O, denoted as m), as molality is not affected by temperature change. Molar units (i.e. Molarity in mol/L-solution, denoted as M) are used for the calculation of pcH. Therefore, solutions in this report are presented in both molality and Molarity.

2.4 Titration Procedure

Titrations were conducted as per SP 12-14 Rev.5 *Use of pH Meters and Electrodes*. The densities of the samples were calculated using mass and volume data collected and reported in Appendix A. The sample in a beaker was placed into a temperature control apparatus (water bath or aluminum bead bath) on a stirring hot plate. The sample was continuously stirred throughout the titration. The temperature (°C) was monitored with a calibrated thermometer throughout the titration. Starting and ending temperatures were recorded for each titration. mV/pH of the electrolyte solution was stabilized to within 5 mV/0.5 pH units for 1-3 minutes before beginning of the titration. Titrations were completed using a digital titration system or by hand, using a pipette (both methods were used in this study). Starting pH was recorded in the Scientific Notebook (SN) and references are documented in the First Milestone report for TP 18-01 (Kirkes, 2020b). The titration system software and the titrator or pipette was set up to deliver the appropriate volume of the titrant. 0.1 M HCl, the titrant used for this study, was loaded into the automatic titrator system (Titrator-1 in Table 2) or placed in a beaker for manual titrations. The titration was terminated when a minimum of 3 pH units of difference was obtained from the starting pH (usually between 2-5 mL of titrant, depending on the system being used and the aliquots of titrant being added). Titration data was obtained from the auto-titrator system.

The titrations were completed using three different liquid junction electrode types, to compare the measured correction factors between different electrodes. The titrations were performed at a minimum a duplicate for each temperature, each electrode and for each solution matrix. The replicates were averaged to produce the final correction factor.

3 Data Analysis

Using Equation 1 the corrected pH, pcH can be calculated. The pcH is determined by known added concentration of H^+ in Molarity, i.e., $[H^+]_{added}$. For NaCl solution, $[H^+]_{added} \equiv [H^+]_{free}$ due to lower buffer capacity of NaCl solution. Equation 1 can be re-arranged into the following:

$$[H^+]_{added} \text{ or } [H^+]_{free}\ (M) = 10^{-A} \times [H^+]_{obs}$$ **Equation 3**

where $[H^+]_{obs} = 10^{-pH_{obs}}$.
Thus, upon re-writing,

$$[H^+]_{obs} = 10^{A} \times [H^+]_{free}\ (M)$$ **Equation 4**

Therefore, A is the base 10 logarithm of the slope of linear regression line through data points in a plot where $[H^+]_{obs}$ are on vertical axis and $[H^+]_{added}$ are on horizontal plot.
The H^+_{free} can be determined through Equation 5:

$$[H^+]_{free} = \frac{V_{added}\,N}{V_i + V_{added}}$$ **Equation 5**

where:

V_i -the volume of brine added to the titration vessel (ml)
V_{added} -the volume of standardized acid addition (ml)
N -the normality of the standardized HCl solution

The brine solutions were prepared in molality and reported in both molality and Molarity. Conversion factor of molality to Molarity, m:M in kg-water/L-solution, is defined in Equation 6 and m:M ratio can be calculated using Equation 7 (Jang (2020)).

$$m \times (m:M) = M$$ **Equation 6**

$$m:M = 1000\rho/[1000 + \Sigma(FW_{solute} \times m_{solute})]$$ **Equation 7**

where:

ρ	-density of solution in g/mL or kg/L
m_{solute}	-molality of a solute
FW_{solute}	-molecular weight of *i* species in g/mol

The conversion of molality to Molarity (m:M) is reported in Appendix A for all the solutions used in this report. The solution densities used in the calculations were reported in Appendix A. Using the conversion factor (m:M), Equation 8 used to convert pcH to pmH.

$$pmH = pcH - \log (M{:}m) \qquad \textbf{\textit{Equation 8}}$$

4 *Tasks and Results*

4.1 Task 1 – Data Assembly and Screening

Data analysis was conducted on the experimental data documented in the First Milestone Report for TP 18-01 (Kirkes, 2020b). Data includes NaCl brines from 1.00 m (0.99 M) – 5.00 m (4.52 M) NaCl at 25 °C and SGWB from 25 to 80 °C. Table 3 lists the solutions and the conditions used to complete the titrations.

Table 3. A list of completed titrations

Solution	Titrant	Increment of Addition	Target Temperature
1.00 m (0.99 M) NaCl	0.1 M HCl	0.05 mL	25 °C
2.00 m (1.92 M) NaCl	0.1 M HCl	0.05 mL	25 °C
3.00 m (2.82 M) NaCl	0.1 M HCl	0.05 mL	25 °C
4.00 m (3.69 M) NaCl	0.1 M HCl	0.05 mL	25 °C
5.00 m (4.52 M) NaCl	0.1 M HCl	0.05 mL	25 °C
SGWB	0.1 M HCl	0.05 mL	25 °C – 80 °C
Note: Data from the First Milestone Report for TP 18-01 (Kirkes, 2020b)			

4.1.1 Summary of collected pcH correction factors

pH correction factors were determined for NaCl brines ranging from 1 m to 5 m and SGWB (0.91 m $MgCl_2$, 3.16 m NaCl) by titrating with HCl. Duplicate titrations were conducted for repeatability and accuracy. Data was acceptable if the final pH correction factor had a standard deviation, within 2 standard deviations of the mean or the standard deviation was lower than 0.01, as documented in Appendix B. The averages of the pH correction factors are listed in Table 4..

Table 4. Average pcH correction factors for TP 18-01

Correction Factors for NaCl Brines at 25 °C			
Concentration	Ross Sure-flow junction	DGi115SC fixed ground-glass sleeve junction	DGi-101SC ceramic frit junction
1 m (0.99 M)	0.202	0.084	-0.054
2 m (1.92 M)	0.408	0.265	0.141
3 m (2.82 M)	0.638	0.425	0.376
4 m (3.69 M)	0.795	0.606	0.526
5 m (4.52 M)	0.999	0.769	0.725
NaCl solutions are from WIPP-pHCOR-1 Pg. 42. Conversions are from Appendix A, Table 9, portion B of this report.			
Correction Factors for SGWB			
Solution/Temperature	Ross Sure-Flow	DGi-115SC	DGi-101SC
SGWB 25 °C	0.915	0.807	0.784
SGWB 30 °C	0.813	0.634	0.851
SGWB 40 °C	0.914	0.621	RR
SGWB 50 °C	0.925	0.789	0.792
SGWB 60 °C	0.948	0.809	RR
SGWB 70 °C	RR	0.880	RR
SGWB 80 °C	0.995	1.030	RR

Note: RR: Re-Ran (this indicates experiments/data that needs to be Re-analyzed)

4.2 Task 2 – Calculation of Apparent K_{app} and $K_{w,app}$

Calculation of apparent K_{app} and $K_{w,app}$ was not applicable for the data reported in the First Milestone Report for TP 18-01 Rev.1 (Kirkes, 2020b).

4.3 Task 3 – Determination of Correction Factors using different electrodes

Table 5 shows a list of electrodes tested in this study and the electrode types used in the literature.

Table 5. Electrodes used for titrations in this study and literature

Electrode/Brand	Junction Type	Internal Reference	Source
Mettler Toledo DGi-115 SC	Ceramic Frit	Ag/AgCl	This Study
Mettler Toledo DGi-101 SC	Fixed Ground Glass Sleeve	Ag/AgCl	This Study
Ross Semi-Micro	Sure-Flow	Pt wire	This Study
Corning Semi-Micro	Ceramic Frit	Ag/AgCl	Roselle, 2011
Fisher Accumet Semi-Micro	Single	Ag/AgCl	Roselle, 2011
Mettler Toledo DGi-111 SC	Ceramic Frit	Ag/AgCl	Roselle, 2011
Orion Ross Semi-Micro	Ceramic Frit	Pt wire	Roselle, 2011
Ross Semi-Micro	Sure-Flow	Pt wire	Roselle, 2011

Orion Ross Semi-Micro	Ceramic Frit	Pt wire	Rai, 1995
Orion Ross	Ceramic Frit	Pt wire	Altmaier, et al 2003
Glass Combination	Single	Ag/AgCl	Borkowski, 2009
Ross Semi-Micro	Sure-Flow	Pt wire	Kirkes and Xiong, 2018

4.3.1 pH correction factor in the NaCl brines

Table 6 shows the data (Kirkes, 2020b), comprising the average calculated pH correction factors for each NaCl concentration and the associated standard deviations. Figure 1 shows the averages of the measured correction factors plotted against the Molarity of the solution, for the three electrodes. All molar concentrations, were calculated using the information in Appendix C.

Table 6. Average correction factor for NaCl brines at 25 °C

NaCl (m)	NaCl (M)	Probe	A	Std. Dev
1.00	0.99		0.084	0.007
2.00	1.92		0.265	0.020
3.00	2.82		0.425	0.008
4.00	3.69	Mettler Toledo	0.606	0.011
5.00	4.52	DGi115-SC	0.769	0.015
1.00	0.99		0.202	0.010
2.00	1.92		0.408	0.027
3.00	2.82		0.638	0.029
4.00	3.69		0.795	0.006
5.00	4.52	Ross, Sure Flow	0.999	0.036
1.00	0.99		-0.054	0.023
2.00	1.92		0.141	0.003
3.00	2.82		0.376	0.031
4.00	3.69	Mettler Toledo	0.526	0.018
5.00	4.52	DGi101-SC	0.725	0.040

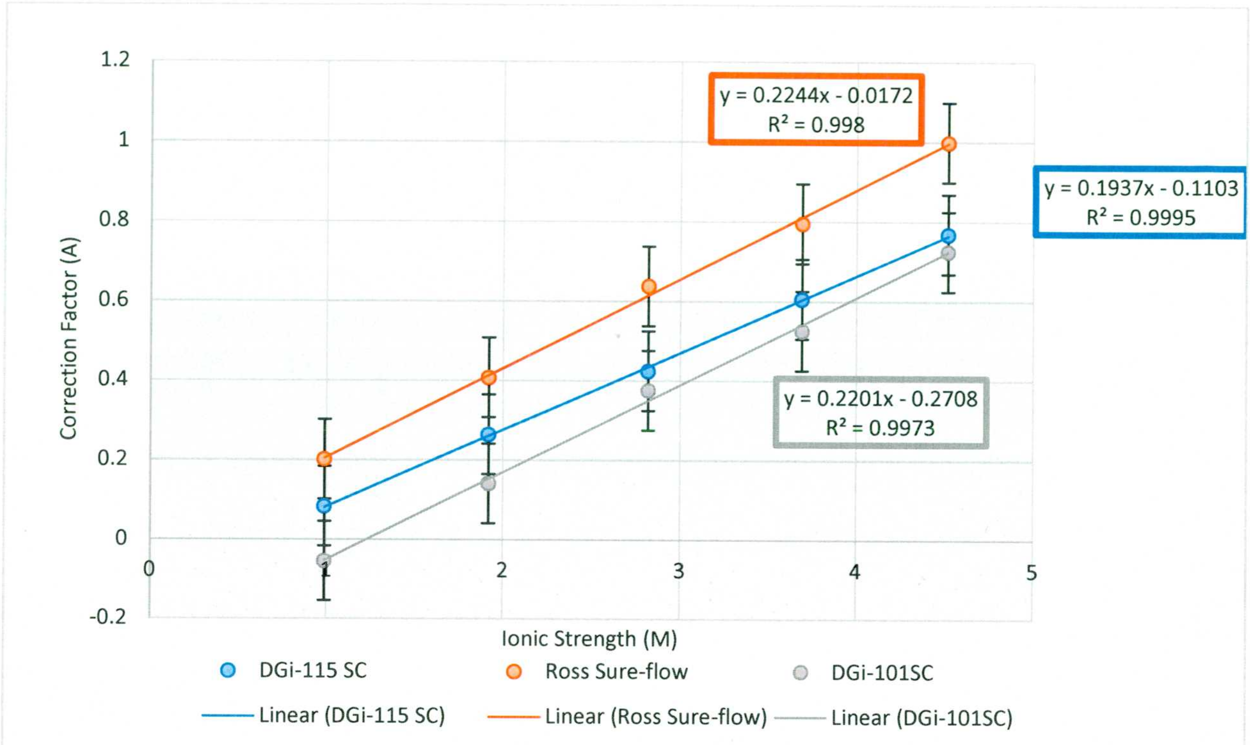


Figure 1. Plot of pH correction factors for NaCl brines at 25 °C. Error bars represent ± 0.1 pH units, as per SP 12-14 Rev.5.

Correction factors are not significantly different for three different electrode types, with the Ross Sure-Flow electrode having the highest correction factors ranging from 0.202 at 1.00 m NaCl to 0.999 at 5.00 m, and the DGi-101SC electrode, having the lowest correction factors ranging from -0.054 at 1.00 m to 0.725 at 5.00 m NaCl. AP-157 Rev.0 (Roselle, 2011) reports data collected on NaCl solutions from 0.05 m to 5.6 m, using several different electrode types, as summarized in Table 5. The data collected in the report by Roselle (2011) is summarized in Table 7.

Roselle (2011) reported solution concentrations in molality, therefore, in Table 7 these data were converted to Molarity using the density information reported in Appendix C.

Table 7 Summary of Roselle, 2011 DataError! Reference source not found.

NaCl (m)	NaCl (M)	Electrode	A
0.10	0.10		-0.052
0.10	0.10		-0.056
1.00	0.99		0.044
1.00	0.99		0.047
3.00	2.82		0.373
3.00	2.82		0.377
5.14	4.63		0.738
5.14	4.63	Corning Semi-Micro Combo	0.741
0.03	0.03		0.007
0.03	0.03		-0.032
0.33	0.33		-0.017
0.33	0.33		-0.038
1.01	1.00		0.000
1.01	1.00		0.062
3.01	2.89		0.348
3.01	2.89		0.415
6.01	5.35		0.983
6.01	5.35		0.951
6.01	5.35	Fisher Accumet Semi-Micro	0.983
0.10	0.10		-0.096
0.10	0.10		-0.076
	1.00		0.009
	1.00		0.030
	1.00		0.000
	1.00		-0.013
	2.00		0.202
	2.00		0.198
	3.00		0.390
5.00	4.52		0.685
5.00	4.52	Mettler Toledo DGi-111SC	0.700
0.01	0.01		-0.020
0.01	0.01		-0.025
0.10	0.10		-0.029
0.10	0.10		-0.028
0.10	0.10		-0.027
0.20	0.20		-0.060
0.50	0.49		0.023
0.50	0.49		0.017
	1.00		0.103
	1.00	Orion Ross Semi-Micro	0.101
0.05	0.05		-0.062
0.05	0.05		-0.062
0.10	0.10	Ross Sure-flow Combination	-0.064

0.10	0.10	-0.062
0.10	0.10	-0.064
1.00	0.98	0.045
1.00	0.98	0.052
2.00	1.92	0.215
2.00	1.92	0.215
3.00	2.82	0.376
3.00	2.82	0.377

Note: Error bar for all data in Roselle, 2011 is reported as ±0.1 pH units.

Figure 2shows pcH correction factors for molar solutions in Roselle, 2011 were plotted against the data collected in this study (Kirkes, 2020b).

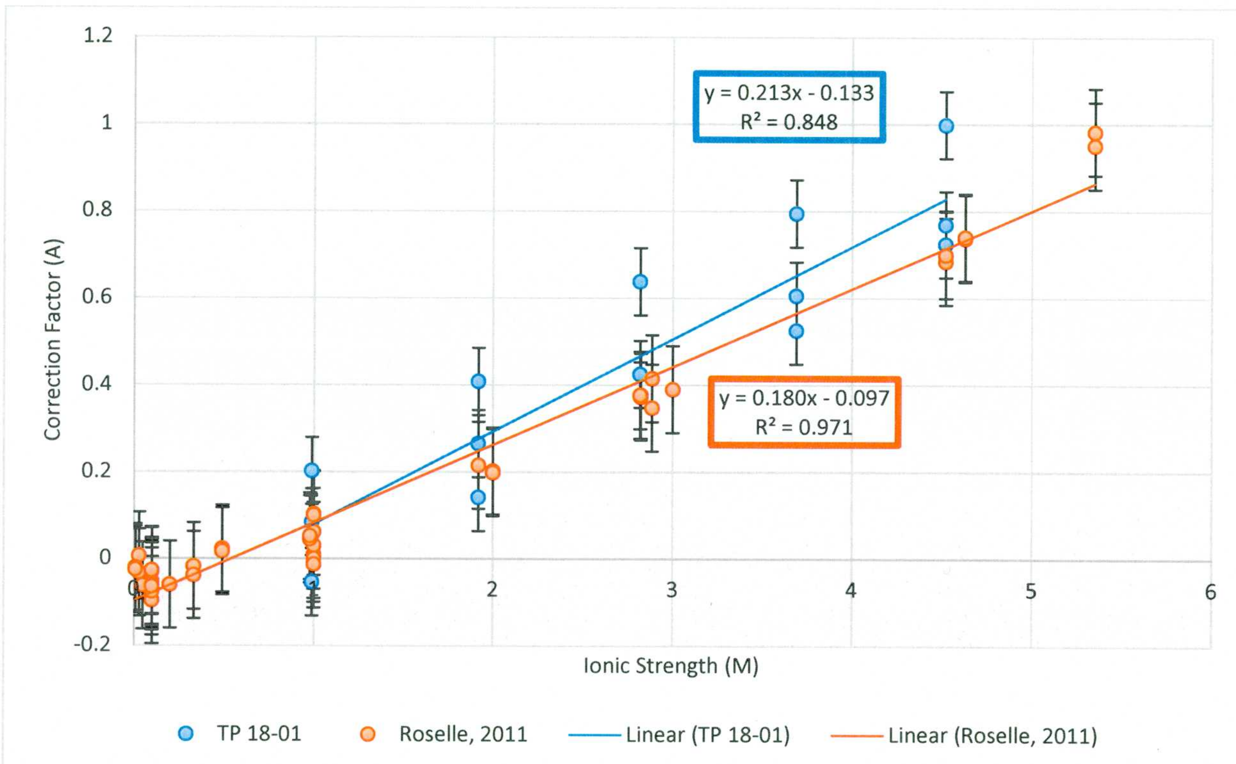


Figure 2. pcH correction factors for NaCl brines at 25 °C by Roselle (2011) and in this study (TP 18-01) and their linear fittings. Error bars represent ±0.1 pH units.

According to Figure 2, the data analyzed in this work (Kirkes, 2020b) at higher ionic strength deviated from the Roselle data. It is noted that pH probes used in two studies were different.

A literature search was completed up to July 2021 to compare the data collected under the same experimental conditions as this study. A few data were found in the literature (Altmaier et al., 2003; Rai et al., 1995; Borkowski et al., 2009). All titrated solutions measured in these studies are reported in both molality and Molarity (as needed to compare to this study) and presented in Table

8. Molarity and molality conversions were completed using the densities in Appendix C. Table 5 contains all electrode information for the listed literature studies. The values in Table 8, reported by Altmaier et al. (2003) were calculated using Equation 9:

$$A_{NaCl} = -0.0988 + 0.1715\, m_{NaCl} + 0.0013\, (m_{NaCl})^2 \qquad \textit{Equation 9}$$

Specific literature studies were included if they adhered to the following criteria:

- pH correction factors were determined for NaCl solutions, only (not mixtures)
- pH correction factors were determined using a modified Gran titration method
- pH correction factors were measured using a commercially available combination electrode at ambient temperature (i.e. ~25 °C).

Table 8. pcH correction factors from literature for NaCl brines (all data collected at ambient conditions)

Correction Factors from Literature at ambient conditions (~25 °C)				
NaCl (m)	**NaCl (M)**	**Electrode**	**A**	**Reference**
1.00	0.99		0.140	
2.00	1.92		0.240	
3.00	2.82		0.480	
4.00	3.69		0.590	
5.00	4.52		0.810	
5.50	4.94		0.920	
6.00	5.35	Orion, Ross Semi-micro	0.970	Rai et al., 1995
0.50	0.50		-0.010	
1.00	0.99		0.070	
2.00	1.92		0.250	
3.00	2.82		0.430	
4.00	3.69		0.610	
5.00	4.52		0.790	
5.60	5.03	Orion, Ross	0.900	Altmaier et al., 2003
	5.00	Glass Combination	0.820	Borkowski et al., 2009

Figure 3 presents the comparison of the pH correction factor for the literature studies and the data from this study.

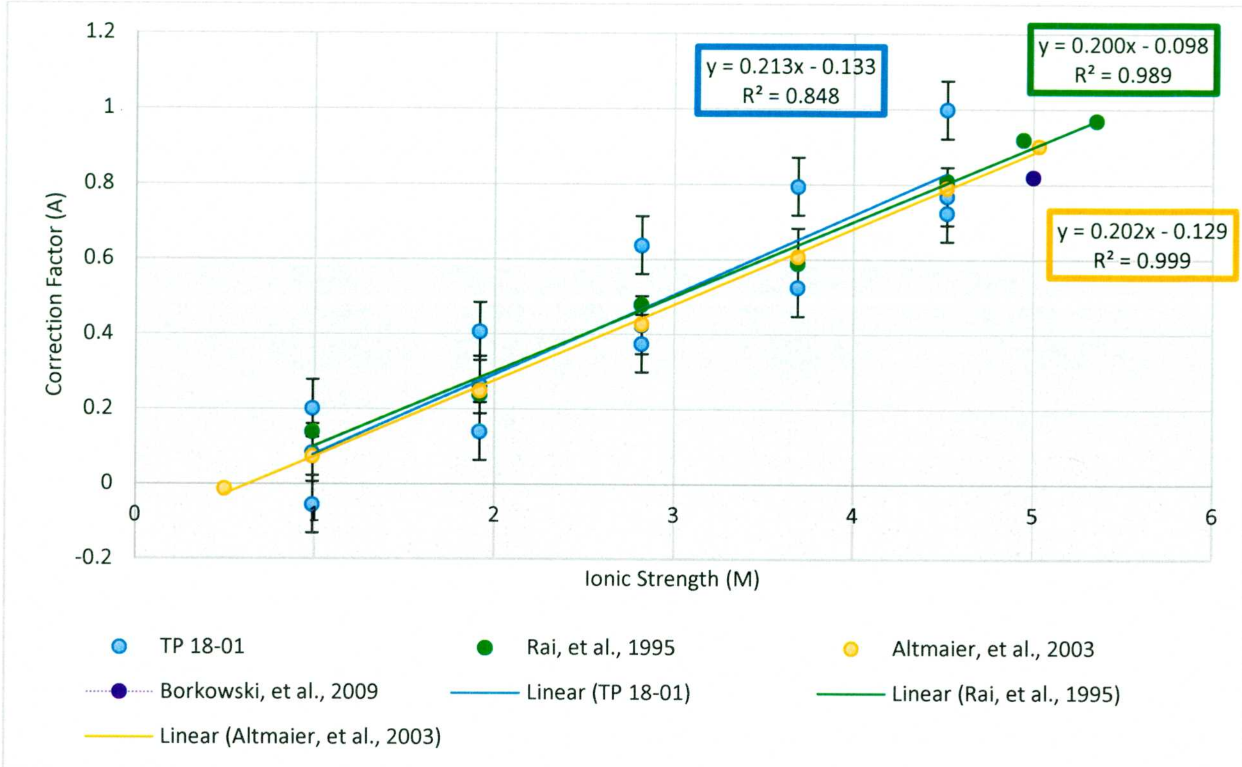


Figure 3. pcH correction factors from literature vs. TP 18-01. Error bars for TP 18-01 data represent ± 0.1 pH units.

The literature data is in agreement with the data collected in this study. The equations derived from the trend lines of the data sets are very similar as demonstrated by the slopes of the linear equations, as shown in Figure 3. The difference is minimum between the various types of electrodes used for the NaCl titrations, as demonstrated in Figure 4. Differences recorded by the various electrodes, are within the error of the pH electrode itself (i.e. ± 0.1 pH unit). These small differences could also be attributed to the relative age of the electrode when the titrations were completed.

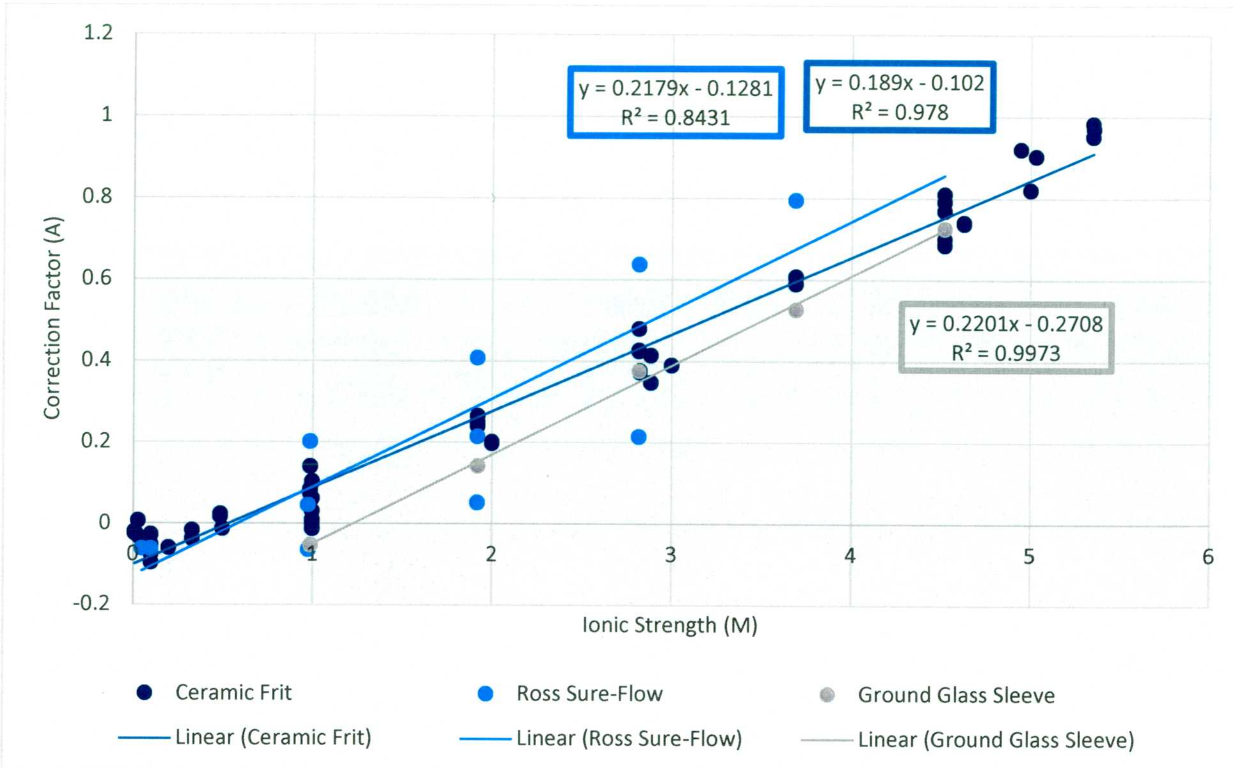


Figure 4. Plotted (A) vs. Ionic Strength (M) by electrode type.

A final scope of this work is to compare experimentally collected pcH correction factors to pcH correction factors derived using EQ3/6 (Harvie et al., 1984; Felmy and Weare, 1986; Wolery and Jarek, 2003). Table 9 shows the data obtained from EQ3/6. The densities, and pcH were calculated by the EQ3/6 code using Data0.FM4 and summarized in Appendix D. Table 9 presents a summary of the calculated pcH correction factors from EQ3/6 and the m to M conversions.

Table 9. Summary of data generated from EQ3/6

	EQ3/6 Calculated pcH	
NaCl, m	NaCl, M	A
0.50	0.50	-0.093
1.00	0.99	-0.030
2.00	1.92	0.136
3.00	2.82	0.327
4.00	3.69	0.531
5.00	4.52	0.744
6.00	5.35	0.963

Note: m to M conversions were completed as per Appendix C

Figure 5 shows the correlation of the pH correction factor (from EQ3/6) vs the calculated Molarity, along with the experimentally collected data from all sources cited in this study. The pH correction factors reported in Appendix D were calculated by subtracting the pcH from pH (NBS scale) calculated by the EQ3/6. (Note: The EQ3/6 software package denotes pH on

National Bureau of Standards (NBS) scale, however in 1988 the NBS became the National Institute of Standards and Technology (NIST)). As shown in Figure 5, the EQ3/6 calculated pcH values are within the 0.1 pH unit acceptance criteria of the pH electrodes. Calculated EQ3/6 values deviate from the measured data at lower ionic strength; however, values are more closely aligned with the measured data at higher ionic strengths.

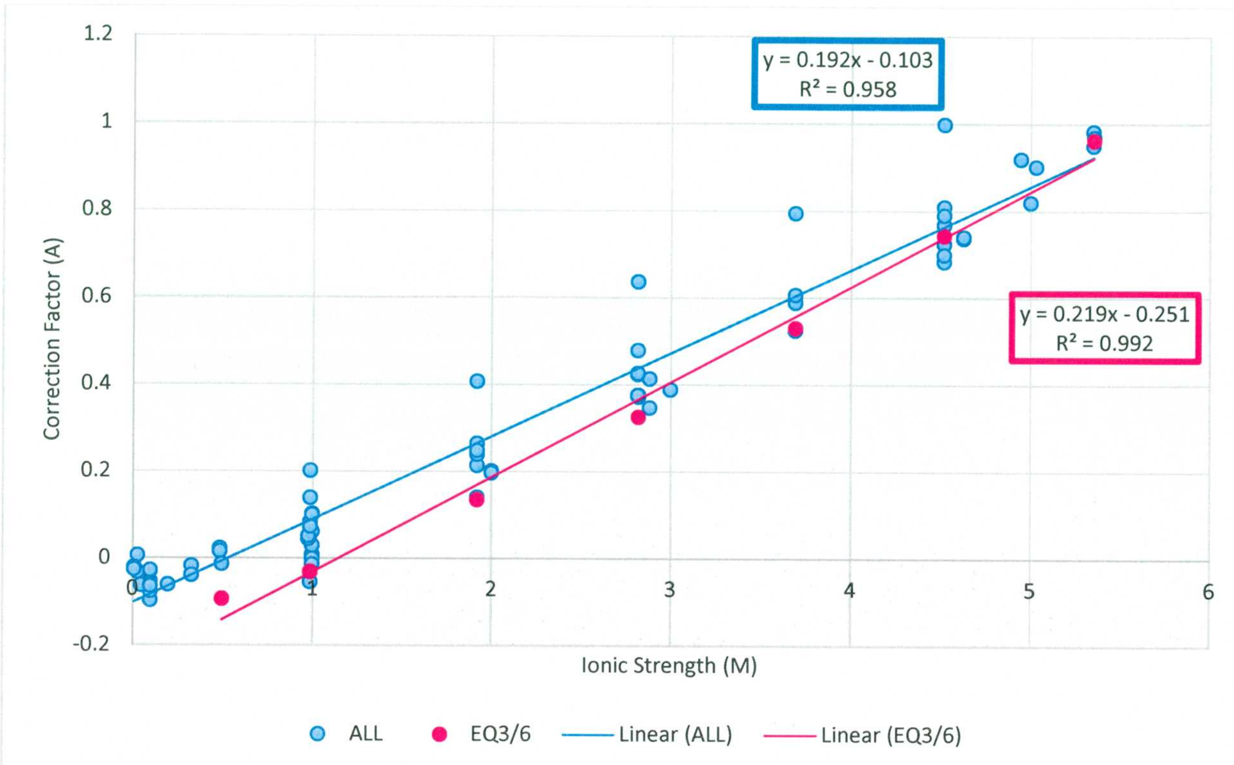


Figure 5. pcH correction factors from all experimental data in this study, literature and calculated by EQ3/6.

Utilizing the data in Figure 5, a generalized equation (Equation 10), was derived for determination of pcH correction factors in NaCl solutions. Since there was minimal difference, as shown in Figure 4 between the various electrode types, all electrode data was used to generate the linear equation, (Equation 10). This equation can be used as a universal equation for pcH correction factor determination for pure NaCl solutions up to 6 m and ambient temperatures.

$$A_{NaCl} = 0.192(I_M) - 0.103 \qquad \textit{Equation 10}$$

4.3.2 SGWB and other SGWB-like brines

SGWB is comprised of a mixture of $MgCl_2$ brine and NaCl brine. SGWB was prepared with $MgCl_2$ at 0.91 m concentration and NaCl at 3.16 m concentration (See Table 11), resulting in an ionic strength of 5.63 M. Concentration and density information for SGWB is presented in Section 4.1.1.

Table 10 shows the numerical data, comprising the average calculated pcH correction factors for each temperature at which SGWB was titrated, for the three electrode types. Figure 6 shows the averages of the measured correction factors plotted against the Molarity of the solution, for the three electrodes that were tested, along with the standard deviations for the measured values.

Table 10. Average pcH correction factors for SGWB at various temperatures

	DGi-115SC	
Solution/Temperature	A	Std. Dev.
SGWB 25 °C	0.807	0.049
SGWB 30 °C	0.634	0.013
SGWB 40 °C	0.621	0.105
SGWB 50 °C	0.789	0.018
SGWB 60 °C	0.809	0.023
SGWB 70 °C	0.880	0.025
SGWB 80 °C	1.030	0.042
	Ross Sure-flow	
SGWB 25 °C	0.915	0.019
SGWB 30 °C	0.813	0.032
SGWB 40 °C	0.914	0.024
SGWB 50 °C	0.925	0.026
SGWB 60 °C	0.948	0.029
SGWB 70 °C	RR	NA
SGWB 80 °C	0.995	0.171
	DGi-101SC	
SGWB 25 °C	0.784	0.048
SGWB 30 °C	0.851	0.003
SGWB 40 °C	RR	NA
SGWB 50 °C	0.792	0.015
SGWB 60 °C	RR	NA
SGWB 70 °C	RR	NA
SGWB 80 °C	RR	NA

Note: RR: Re-Rans, this indicates experiments that need to be Re-analyzed

In order to directly compare data obtained for the NaCl solutions and the data obtained for the SGWB solutions, all solutions are presented in ionic strength on a Molarity basis. Ionic strength was calculated using Equation 11:

$$I = \frac{1}{2}\sum_{i} c_i z_i^2 \qquad \textbf{\textit{Equation 11}}$$

where:

I -ionic strength

c_i -concentration of the i^{th} ion

z_i^2 -the charge of i^{th} ion

The calculated ionic strengths for all NaCl solutions are summarized in Appendix C. Table 11 summarizes the information for the SGWB used in this study. The corrected molality for SGWB represents the nominal values for $MgCl_2 \cdot 6H_2O$ and NaCl in the prepared solution.

Table 11. The calculation of ionic strength of SGWB brine from a lab preparation recipe

SGWB		
	$MgCl_2 \cdot 6H_2O$	**NaCl**
Target molality	1.00	3.50
Grams of $MgCl_2$ added	409.60	409.08
grams of water from salt	217.78	0.00
grams of water measured	2000.00	2000.00
Total Water, mL	2217.78	2217.78
Total Water, L	2.22	2.22
CORRECTED, m	**0.91**	**3.16**
Density, g/mL	1.0652	1.1097
Conversion of m to M	0.89	2.96
Based on the numbers listed above the Ionic Strength for SGWB is calculated as **5.63 M.**		

Note: The densities used to convert the solutions from m to M are calculated using the figures in Appendix C. Significant figures represent a reading directly from an instrument or relative significant figures for these values.

Figure 6 presents the pcH correction factors measured for SGWB at 25 °C for the three electrodes used in this study and those measured for NaCl in all cited sources. The pcH correction factors obtained for the SGWB were lower than that seen for the pure NaCl solutions as shown in Figure 6.

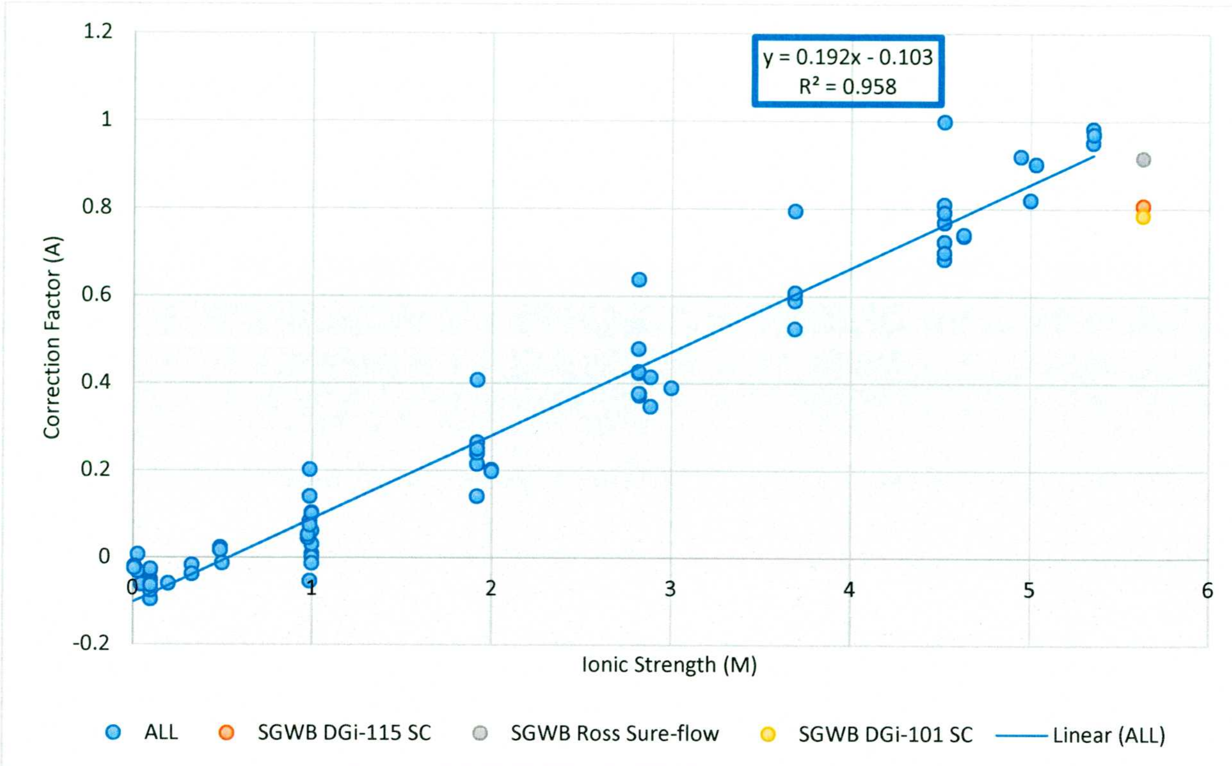


Figure 6. pcH correction factors for SGWB vs NaCl from all sources at 25 °C.

A literature review was completed to compare the SGWB titration results in this study, similar to the solutions in the literature. Specific literature studies were included if they adhered to the following criteria:

- pcH correction factors were determined for simple mixed brines, similar to SGWB (i.e. NaCl and $MgCl_2$ dominated brines).
- pcH correction factors were determined using a modified Gran titration method
- pcH correction factors were measured using a commercially available combination electrode at ambient temperature (i.e. ~25 °C).

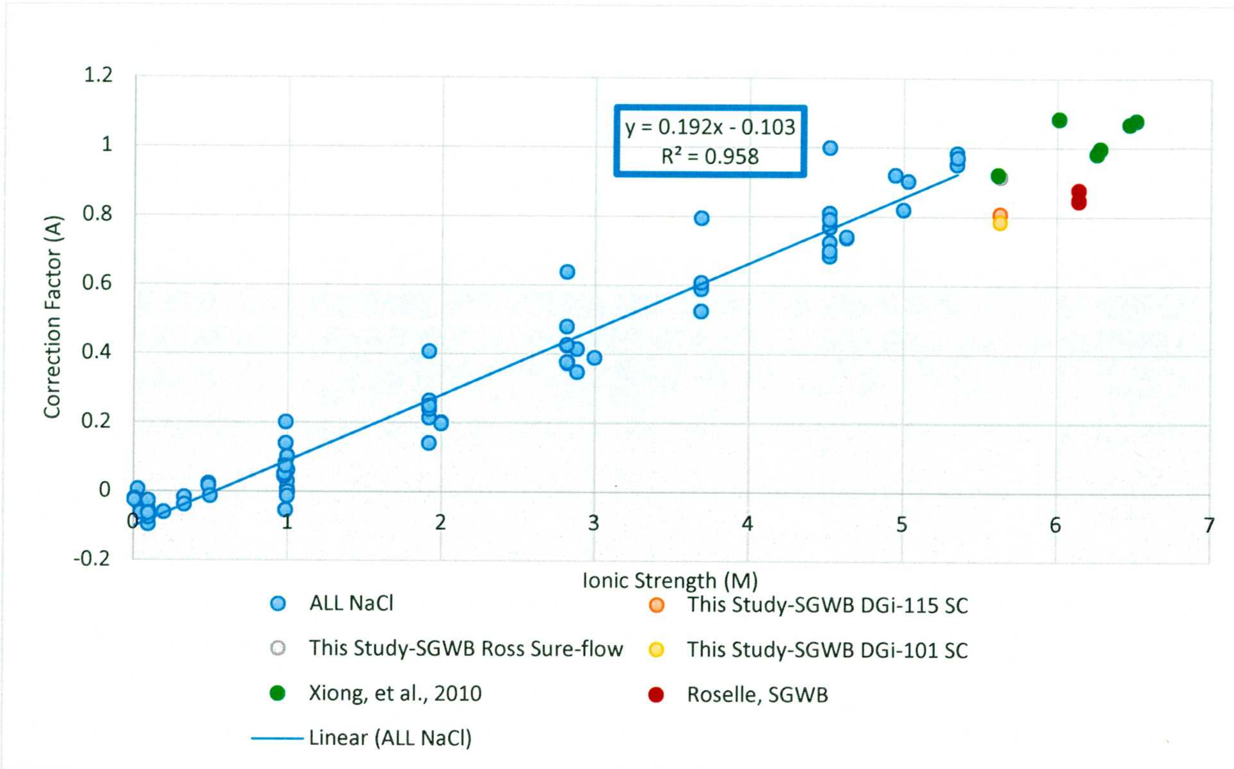


Figure 7. pcH correction factors for SGWB-like brines vs NaCl at 25 °C.

Figure 7 shows the titration data collected from SGWB-like brines from this study and the literature. SGWB-like data represented in Figure 7 are from Xiong et al. (2010), Roselle (2011) and this study. All the literature brines contained varying concentrations of NaCl brine and $MgCl_2$ brine in a simple complex. The ionic strength values in the work by Xiong et al. (2010) were calculated and are presented in Appendix C. Conversions of the solutions from m to M, and the densities used for those conversions are presented in Appendix C. Figure 8 shows the trend line calculation for all SGWB-like data vs the NaCl (data include only the pcH correction factors at 25 °C).

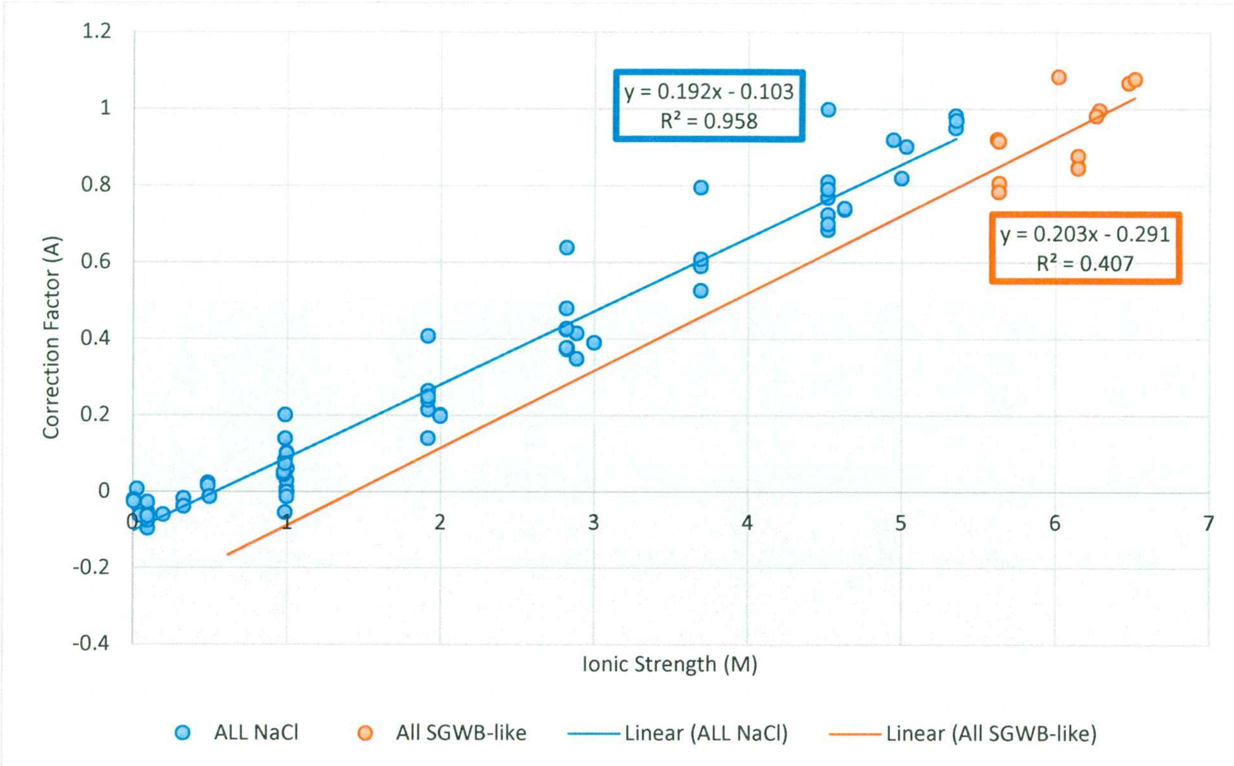


Figure 8. Comparison of pcH correction factors for SGWB-like solutions to NaCl solutions at 25 °C.

From Figure 8 an equation can be generated to determine pcH correction factors in simple mixed solutions containing NaCl and $MgCl_2$ brines at 25 °C. In these simple brines NaCl ranged from 0.5 – 5 m, and $MgCl_2$ ranged from 0.5 – 2 m. The equation that can be used for determination of simple solutions containing $MgCl_2$ and NaCl at 25°C is:

$$A_{SGWB} = 0.203(I_M) - 0.291 \qquad \textit{Equation 12}$$

The equation generated is very similar to the equation for NaCl pure solutions, however, the derived correction factors are slightly lower according to Figure 8.

4.3.3 SGWB pcH correction factors at elevated temperatures

SGWB (3.16 m NaCl, 0.91 m $MgCl_2$) was titrated at various temperatures (30 to 80 °C) to determine pH correction factors based on temperature change. Since the activity of H^+ ion is temperature dependent, the change in temperature will affect the pH_{obs}. This study evaluated the simultaneous effects of temperature and high ionic strength on the measured pH Table 12 presents the average pcH correction factor obtained at each temperature in SGWB for each electrode tested in this study. Standard deviations and details of data collection are reported in Appendix B.

Table 12. SGWB Average pcH correction factors

Solution/Temp	ROSS Sure-Flow A	DGi-115SC A	DGi-101SC A
SGWB 25 °C	0.915	0.807	0.784
SGWB 30 °C	0.813	0.634	0.851
SGWB 40 °C	0.914	0.621	RR
SGWB 50 °C	0.925	0.789	0.792
SGWB 60 °C	0.948	0.809	RR
SGWB 70 °C	RR	0.880	RR
SGWB 80 °C	0.995	1.030	RR

Note: RR: Re-Ran (this indicates data that needs to be Re-analyzed)

"RR" notation indicates experiments that need to be Re-Ran (re-analyzed) and will be reported when data will be available. Data was flagged for RR because the results were not within the expected range. Figure 9 shows the graphic representation of the data in Table 12.

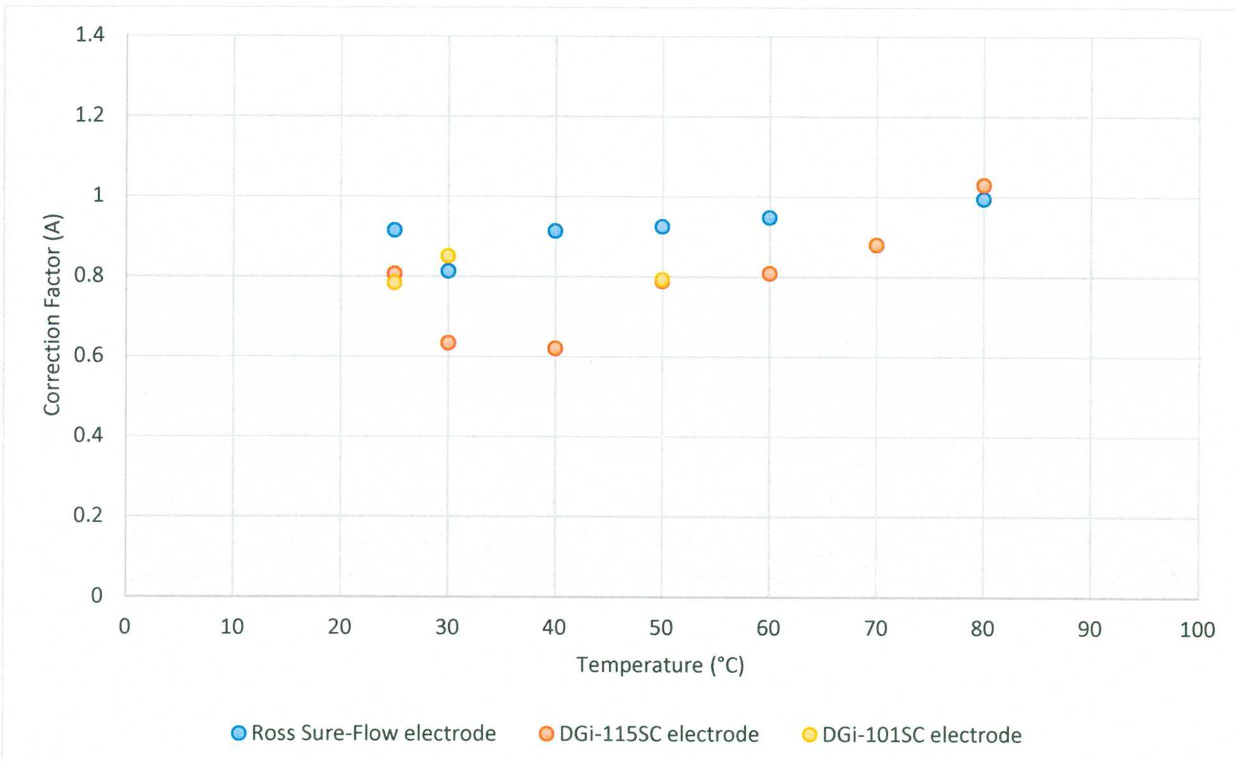


Figure 9. SGWB pH correction factors at evaluated temperatures

The majority of the pH correction factors remained fairly consistent across the measured temperatures, however there was a slight decrease in pH correction factor from 25 °C to 30 and 40 °C. This decrease in pH correction factor at 30 and 40°C was more pronounced in the DGi-115SC electrode, indicating this electrode may be more sensitive to temperature fluctuations. There was not enough data available to clearly delineate a trend for the DGi-101SC electrode. These data were compared to data reported in the literature. One study was found (Kirkes and Xiong, 2018) that measured pH correction factors in NaCl solutions ranging from 1 m to 5.6 m

(1-5 M) and temperatures from 40 °C to 80 °C as shown in Table 13. The data reported in Kirkes and Xiong, 2018 is summarized in Table 13.

Table 13. pH correction factors from Kirkes and Xiong (2018)

Temperature, °C	**NaCl, mol•kg^{-1}**	**A_M**	**A_m**
40	1.0	0.007	–0.00469
	2.1	0.191	0.170
	3.2	0.363	0.332
	4.4	0.564	0.522
	5.6	0.762	0.708
50	1.0	–0.01	–0.0237
	2.1	0.237	0.214
	3.2	0.372	0.338
	4.4	0.579	0.535
	5.6	0.750	0.695
60	1.0	0.08	0.0641
	2.1	0.218	0.192
	3.2	0.433	0.398
	4.4	0.637	0.590
	5.6	0.758	0.700
70	1.0	0.121	0.105
	2.1	0.238	0.212
	3.2	0.429	0.394
	4.4	0.597	0.550
	5.6	0.770	0.712
80	1.0	0.124	0.103
	2.1	0.251	0.221
	3.2	0.457	0.417
	4.4	0.615	0.564
	5.6	0.713	0.651

Note: A_M and A_m are correction factors for pcH and pmH respectively. This image was taken directly from the cited resource (Kirkes and Xiong 2018) and was not re-produced by the authors of this AR.

The pH correction factors by Kirkes and Xiong (2018) were presented in both pcH and pmH. The study reported the universal equations derived for each temperature. Figure 10 shows the literature data in comparison to the data collected in this study.

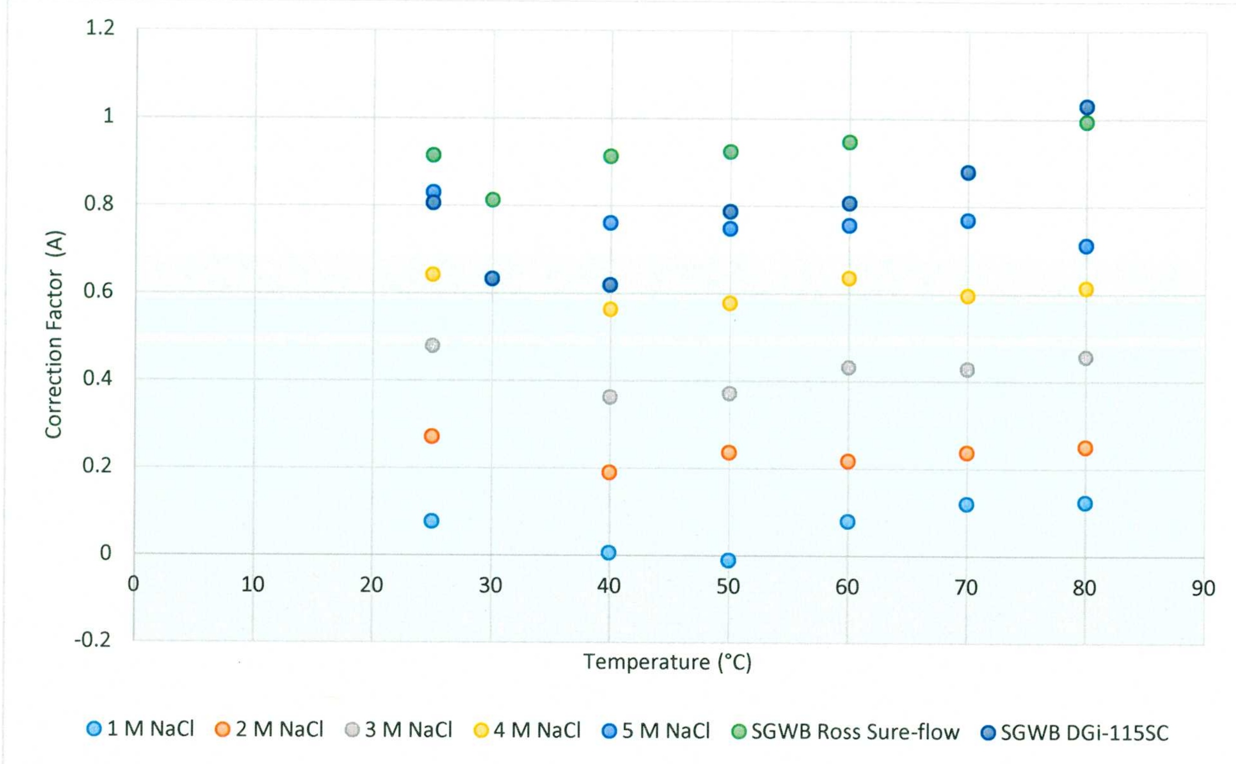


Figure 10. pH correction factors vs Temperature in literature and this study

In Figure 10, the correction factor values at 25 °C is an average of all NaCl measured pH correction factors (from all electrodes) from this study. The 1 M to 5 M NaCl at 40-80 °C data is from the previous work (Kirkes and Xiong, 2018) while those for SGWB are from this study. As shown in the Figure 10, the data trend is very similar to that seen in Figure 9, with a slight negative deviation in pH correction factor from 25 °C to 40 °C, with a minor increase from 40°C to 80°C in most solutions.

The data from this study was also plotted as ionic strength vs pH correction with the literature data, in order to obtain a universal equation for use at the various temperatures (40-80 °C). Figure 11 shows the literature data vs the pH correction factors determined in this study.

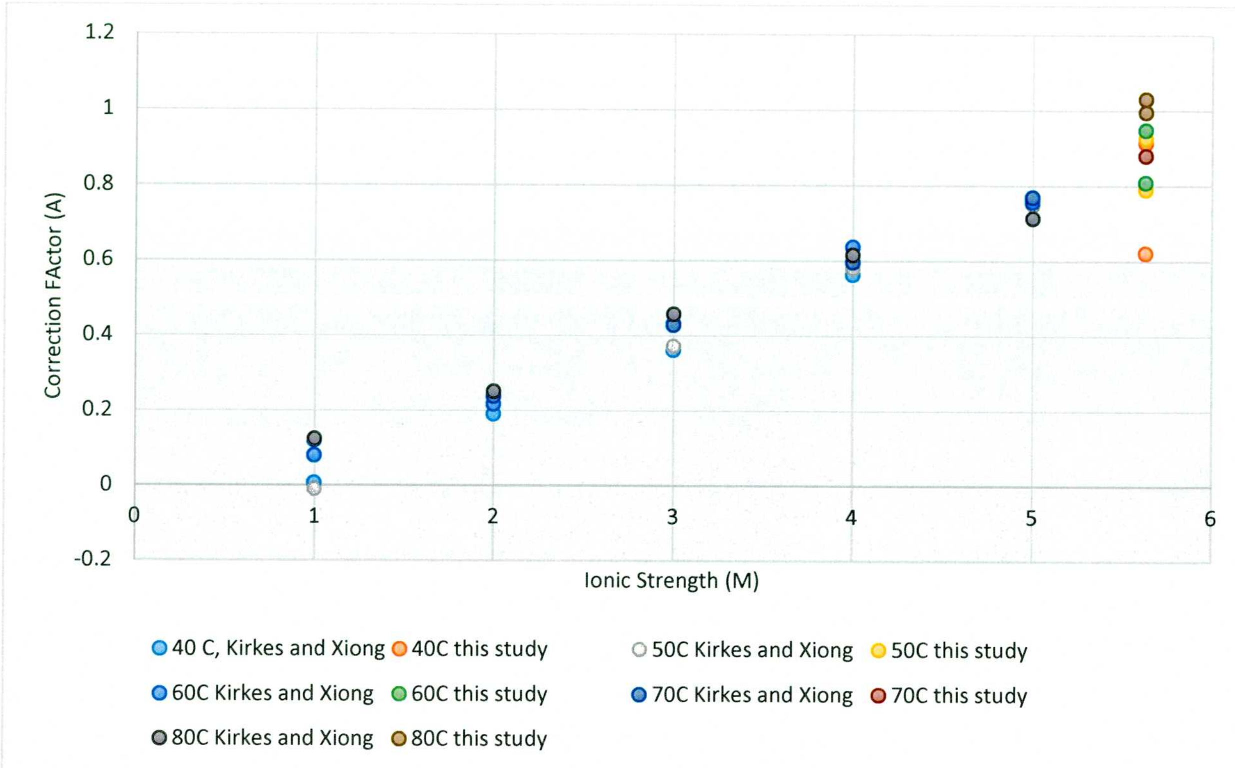


Figure 11. pH correction factors, literature vs this study.

While the pH correction factors in this study showed good agreement with the literature data, it is evident that there is a large difference in the measured pH correction factors between the two electrode types used in this study. The data obtained from the Ross Sure-flow electrode is more consistent with the literature data however, the DGi-115SC electrode data is more deviated, because this electrode is more sensitive to temperature changes. Ross electrode data was reproduced in Figure 12. Figure 12 shows the newly generated graph, excluding the DGi-115SC data.

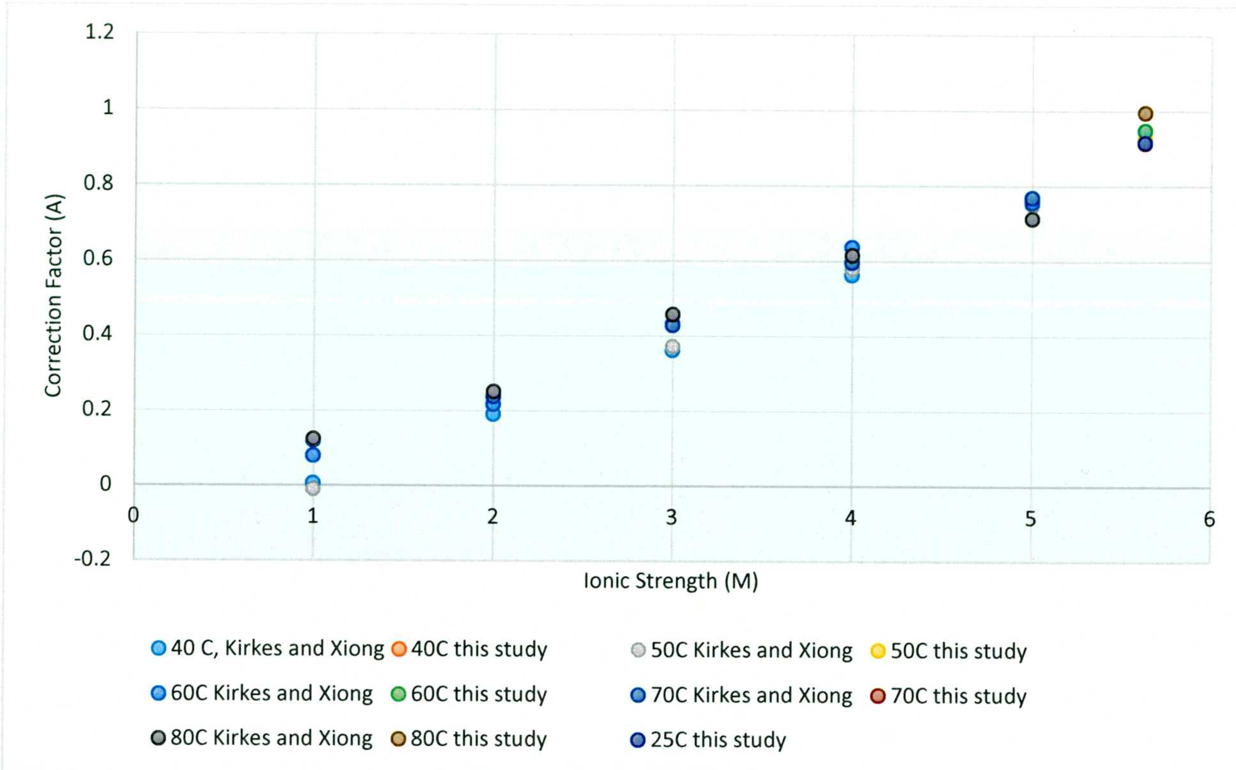


Figure 12. pH correction factors, literature vs this study (DGi-115SC electrode data excluded).

With the DGi-115SC electrode data removed, an equation can be developed to model the data for this simple brine system (SGWB-like) at various temperatures. Figure 13 below shows the literature data and data from this study. According to the findings in this study, the ionic strength effect on the pH correction factor is greater than the effect of temperature.

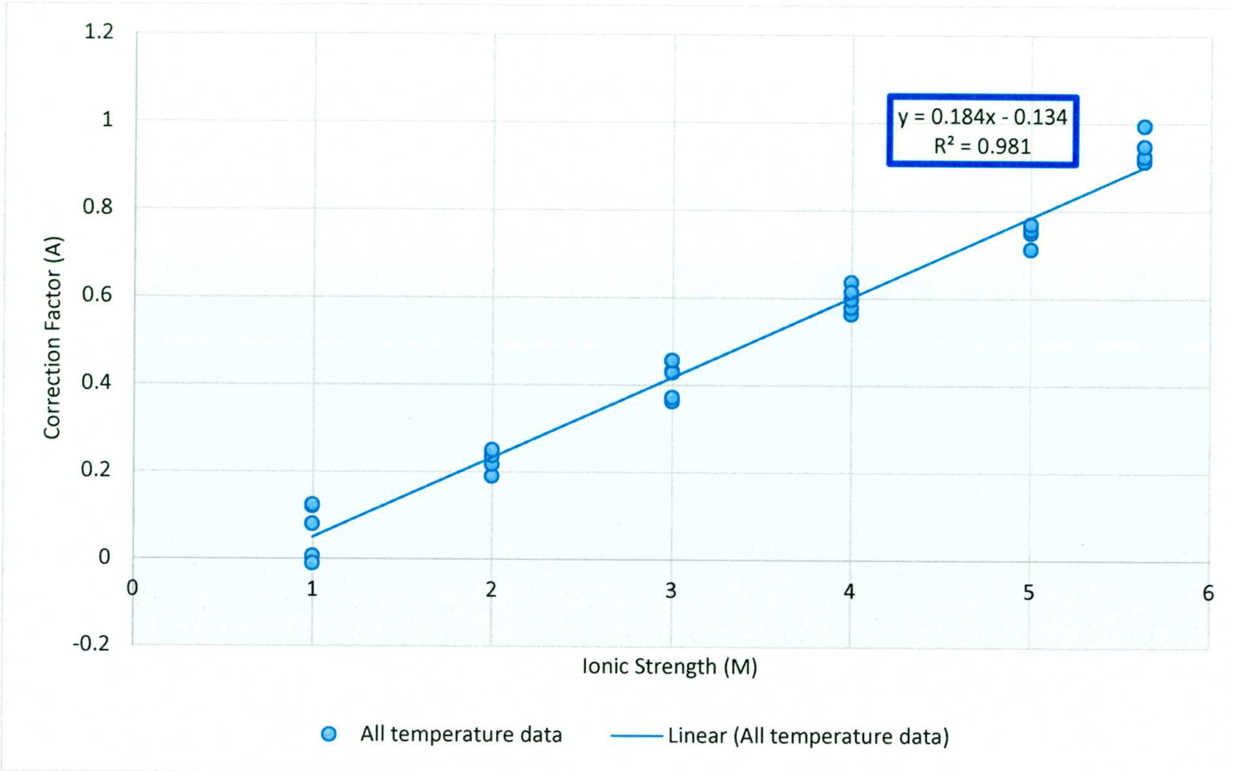


Figure 13. pH correction factors for simple brines at elevated temperatures from 40-80C.

From the data plotted in Figure 13, an equation can be developed to determine pH correction factors for SGWB-like brines at elevated temperatures:

$$A_{SGWB-like} = 0.184(I_M) - 0.134$$

Equation 13

This equation can be used to determine pH correction factors for simple brines containing $MgCl_2$ and NaCl at temperatures from 40 to 80 °C.

4.4 Task 4 – Application of Results

In this report, three equations were derived as follows:

NaCl brines for 25 °C by Equation 10:

$$A_{NaCl} = 0.192(I_M) - 0.103$$

SGWB-like brine (0.91 m $MgCl_2$, 3.16 m NaCl) for 25 °C by Equation 12:

$$A_{SGWB} = 0.203(I_M) - 0.291$$

SGWB-like brines ($NaCl+MgCl_2$) at elevated temperatures (40-80 °C) by Equation 13:

$$A_{SGWB-like} = 0.184(I_M) - 0.134$$

As experimental data was collected for TP 18-01 on the listed tasks in Table 1, additional ARs will be produced to analyze that data. These results will also be used to formulate a unified procedure for determining pH correction factors from observed pH values and if possible, generating universal equations to calculate pH correction factors for tested solutions. Literature data will also be incorporated into these ARs where available. Additional equations will be developed for more complex solutions, as data becomes available.

4.5 Summary

In summary, the three pH correction factor equations above obtained in this report are overlaid on the equation for pH correction factors presented in Roselle (2011) with uncertainty illustrated in Figure 14 below.

$$A_{NaCl}(\pm 0.47) = 0.186 I_M - 0.150$$

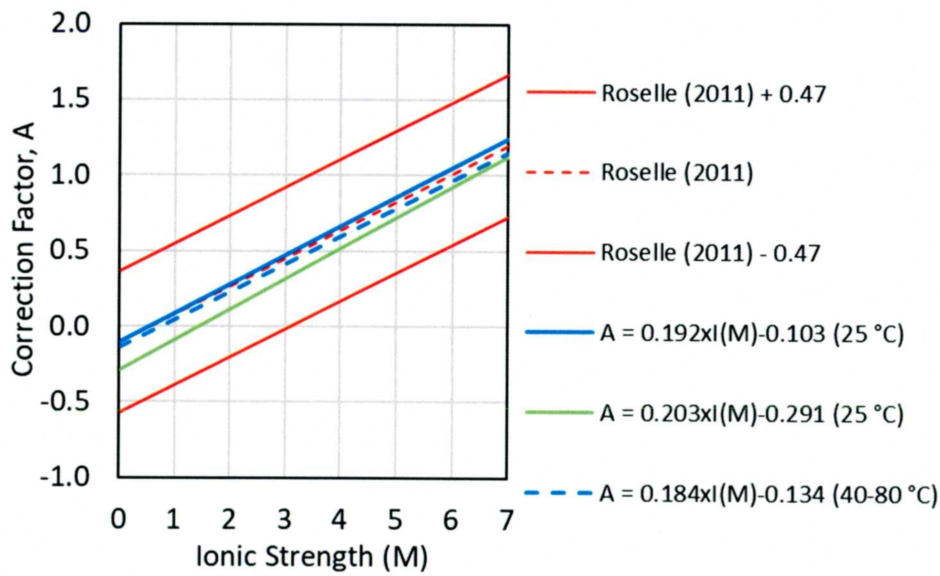


Figure 14. Comparison of A obtained in this AR with Roselle (2011).

The brines analyzed in this report is encompassed by the equation presented in Roselle (2011) within the uncertainty therein, including the pH correction factor obtained at elevated temperature. The uncertainty of Roselle (2011) is as wide as ±0.47, because wider range of brine types are investigated therein to conclude a universal equation for pH correction factor.

Data files associated with this AR can be found at the following file path: CVS/CVSLIB/WIPP EXTERNAL/AP157.

APPENDIX A: *Measured Solution Densities*

Table A1: NaCl Measured Densities

Sample Name	Weight of 50mL of sample (g)	Density	Reference
	Mettler DGi-115 electrode		
1 m NaCl 1 25C	51.7267	1.0345	WIPP-pHCor-2 Pg. 54-55
1 m NaCl 2 25C	51.6884	1.0338	WIPP-pHCor-2 Pg. 54-55
1 m NaCl 3 25C	51.5665	1.0313	WIPP-pHCor-2 Pg. 54-55
	Ross electrode		
1 m NaCl 1 25C	51.3832	1.0277	WIPP-pHCor-1 Pg. 42
1 m NaCl 2 25C	51.5156	1.0303	WIPP-pHCor-1 Pg. 42
1 m NaCl 3 25C	51.5480	1.0310	WIPP-pHCor-1 Pg. 42
	Mettler DGi-101 electrode		
1 m NaCl 1 25C	51.4929	1.0299	WIPP-pHCor-1 Pg. 93
1 m NaCl 2 25C	51.4814	1.0296	WIPP-pHCor-1 Pg. 93
1 m NaCl 3 25C	51.5084	1.0302	WIPP-pHCor-1 Pg. 93
	1 m NaCl Density	1.0309	
	Standard Deviation	0.0020	

Sample Name	Weight of 50mL of sample (g)	Density	Reference
	Mettler DGi-115 electrode		
2 m NaCl 1 25C	53.2024	1.0640	WIPP-pHCor-2 Pg. 55
2 m NaCl 2 25C	53.1901	1.0638	WIPP-pHCor-2 Pg. 55
2 m NaCl 3 25C	53.4159	1.0683	WIPP-pHCor-2 Pg. 55
	Ross electrode		
2 m NaCl 1 25C	53.3083	1.0662	WIPP-pHCor-1 Pg. 49
2 m NaCl 2 25C	53.2820	1.0656	WIPP-pHCor-1 Pg. 49
2 m NaCl 3 25C	53.2942	1.0659	WIPP-pHCor-1 Pg. 49
	Mettler DGi-101 electrode		
2 m NaCl 1 25C	53.3300	1.0666	WIPP-pHCor-1 Pg. 94
2 m NaCl 2 25C	53.3443	1.0669	WIPP-pHCor-1 Pg. 94
2 m NaCl 3 25C	53.2535	1.0651	WIPP-pHCor-1 Pg. 94
	2 m NaCl Density	1.0658	
	Standard Deviation	0.0013	

Sample Name	Weight of 50mL of sample (g)	Density	Reference
	Mettler DGi-115 electrode		
3 m NaCl 1 25C	54.8855	1.0977	WIPP-pHCor-2 Pg. 55-56
3 m NaCl 2 25C	54.9717	1.0994	WIPP-pHCor-2 Pg. 55-56
3 m NaCl 3 25C	54.9146	1.0983	WIPP-pHCor-2 Pg. 55-56
	Ross electrode		
3 m NaCl 1 25C	55.0195	1.1004	WIPP-pHCor-1 Pg. 49
3 m NaCl 2 25C	54.9903	1.0998	WIPP-pHCor-1 Pg. 50
3 m NaCl 3 25C	55.1010	1.1020	WIPP-pHCor-1 Pg. 50
	Mettler DGi-101 electrode		
3 m NaCl 1 25C	54.9053	1.0981	WIPP-pHCor-1 Pg. 94-95
3 m NaCl 2 25C	54.9965	1.0999	WIPP-pHCor-1 Pg. 94-95
3 m NaCl 3 25C	54.8609	1.0972	WIPP-pHCor-1 Pg. 94-95

3 m NaCl Density 1.0992

Standard Deviation 0.0014

Sample Name	Weight of 50mL of sample (g)	Density	Reference
	Mettler DGi-115 electrode		
4 m NaCl 1 25C	56.5560	1.1311	WIPP-pHCor-2 Pg. 56
4 m NaCl 2 25C	56.5672	1.1313	WIPP-pHCor-2 Pg. 56
4 m NaCl 3 25C	56.4823	1.1296	WIPP-pHCor-2 Pg. 56
	Ross electrode		
4 m NaCl 1 25C	56.6421	1.1328	WIPP-pHCor-1 Pg. 51-52
4 m NaCl 2 25C	56.6164	1.1323	WIPP-pHCor-1 Pg. 51-52
4 m NaCl 3 25C	56.6177	1.1324	WIPP-pHCor-1 Pg. 51-52
	Mettler DGi-101 electrode		
4 m NaCl 1 25C	56.5996	1.1320	WIPP-pHCor-1 Pg. 94-95
4 m NaCl 2 25C	56.6113	1.1322	WIPP-pHCor-1 Pg. 94-95
4 m NaCl 3 25C	56.5996	1.1320	WIPP-pHCor-1 Pg. 94-95

4 m NaCl Density 1.1318

Standard Deviation 0.0009

Sample Name	Weight of 50mL of sample (g)	Density	Reference
	Mettler DGi-115 electrode		
5 m NaCl 1 25C	58.0949	1.1619	WIPP-pHCor-2 Pg. 57
5 m NaCl 2 25C	57.9998	1.1600	WIPP-pHCor-2 Pg. 57
5 m NaCl 3 25C	57.9701	1.1594	WIPP-pHCor-2 Pg. 57
	Ross electrode		
5 m NaCl 1 25C	58.1323	1.1626	WIPP-pHCor-1 Pg. 51-52
5 m NaCl 2 25C	58.0802	1.1616	WIPP-pHCor-1 Pg. 51-52
5 m NaCl 3 25C	58.0802	1.1616	WIPP-pHCor-1 Pg. 51-52
	Mettler DGi-101 electrode		
5 m NaCl 1 25C	57.9616	1.1592	WIPP-pHCor-1 Pg. 96
5 m NaCl 2 25C	58.0780	1.1616	WIPP-pHCor-1 Pg. 96

5 m NaCl 3 25C	57.9575	1.1592	WIPP-pHCor-1 Pg. 96
	5 m NaCl Density	1.1608	
	Standard Deviation	0.0013	

Table A2: SGWB Measured Densities

Sample Name	Weight of 50mL of sample (g)	Density	Reference
Mettler DGi-115 electrode			
SGWB 25C 1	58.3415	1.1668	WIPP-pHCor-1 Pg. 23
SGWB 25C 2	58.7160	1.1743	WIPP-pHCor-1 Pg. 18-19
SGWB 25C 3	58.9549	1.1791	WIPP-pHCor-1 Pg. 18-19
SGWB 25C 4	58.9994	1.1800	WIPP-pHCor-1 Pg. 18-19
SGWB 30C 1	57.8763	1.1575	WIPP-pHCor-1 Pg. 39-40
SGWB 30C 2	57.8861	1.1577	WIPP-pHCor-1 Pg. 39-40
SGWB 30C 3	57.8826	1.1577	WIPP-pHCor-1 Pg. 39-40
SGWB 40C 1	59.0184	1.1804	WIPP-pHCor-1 Pg. 20
SGWB 40C 2	58.9515	1.1790	WIPP-pHCor-1 Pg. 20
SGWB 40C 3	58.9769	1.1795	WIPP-pHCor-1 Pg. 20
SGWB 40C RR1	57.7997	1.1560	WIPP-pHCor-1 Pg. 41-42
SGWB 40C RR2	57.8504	1.1570	WIPP-pHCor-1 Pg. 41-42
SGWB 50C 1	59.0145	1.1803	WIPP-pHCor-1 Pg. 21-22
SGWB 50C 2	58.9538	1.1791	WIPP-pHCor-1 Pg. 21-22
SGWB 50C 3	59.0117	1.1802	WIPP-pHCor-1 Pg. 21-22
SGWB 60C 1	59.0097	1.1802	WIPP-pHCor-1 Pg.14-15
SGWB 60C 2	58.9565	1.1791	WIPP-pHCor-1 Pg.14-15
SGWB 60C 3	58.8915	1.1778	WIPP-pHCor-1 Pg.14-15
SGWB 70C 1	58.9617	1.1792	WIPP-pHCor-1 Pg.15-16
SGWB 70C 2	58.9574	1.1791	WIPP-pHCor-1 Pg.15-16
SGWB 70C 3	58.9915	1.1798	WIPP-pHCor-1 Pg.15-16
SGWB 80C 1	58.9752	1.1795	WIPP-pHCor-1 Pg.17-18
SGWB 80C 2	58.9982	1.1800	WIPP-pHCor1 Pg.17-18
Sample Name	**Weight g**	**Density**	**Reference**
Ross Sure-flow electrode			
SGWB 25C 1	57.8526	1.1571	WIPP-pHCor-Pg. 24-25
SGWB 25C 2	57.9076	1.1582	WIPP-pHCor-Pg. 24-25
SGWB 25C 3	57.7690	1.1554	WIPP-pHCor-Pg. 24-25
SGWB 30C 1	57.9360	1.1587	WIPP-pHCor-1 Pg. 38-39
SGWB 30C 2	57.9565	1.1591	WIPP-pHCor-1 Pg. 38-39
SGWB 30C 3	57.9293	1.1586	WIPP-pHCor-1 Pg. 38-39
SGWB 40C 1	57.8036	1.1561	WIPP-pHCor-1 Pg. 26-27
SGWB 40C 2	57.8816	1.1576	WIPP-pHCor-1 Pg. 26-27
SGWB 40C 3	57.8413	1.1568	WIPP-pHCor-1 Pg. 26-27
SGWB 50C 1	57.8330	1.1567	WIPP-pHCor-1 Pg. 28-29
SGWB 50C 2	57.8900	1.1578	WIPP-pHCor-1 Pg. 28-29
SGWB 50C 3	57.9645	1.1593	WIPP-pHCor-1 Pg. 28-29
SGWB 60C 1	57.7681	1.1554	WIPP-pHCor-Pg. 30-31

SGWB 60C 2	57.8315	1.1566	WIPP-pHCor-Pg. 30-31
SGWB 60C 3	57.8745	1.1575	WIPP-pHCor-Pg. 30-31
SGWB 80C 1	57.9112	1.1582	WIPP-pHCor-Pg. 35-37
SGWB 80C 2	57.9560	1.1591	WIPP-pHCor-Pg. 35-37
SGWB 80C 3	57.8201	1.1564	WIPP-pHCor-Pg. 35-37
SGWB 80C 4	57.9635	1.1593	WIPP-pHCor-Pg. 35-37
Sample Name	**Weight g**	**Density**	**Reference**
Mettler DGi-101 electrode			
SGWB 25C 1	57.8519	1.1570	WIPP-pHCOR-2 Pg. 42
SGWB 25C 2	57.8228	1.1565	WIPP-pHCOR-2 Pg. 42
SGWB 25C 3	57.8601	1.1572	WIPP-pHCOR-2 Pg. 42
SGWB 30C 1*	57.7854	1.1557	WIPP-pHCOR-2 Pg. 24
SGWB 30C 2	57.8725	1.1575	WIPP-pHCOR-2 Pg. 24
SGWB 30C 3	57.9488	1.1590	WIPP-pHCOR-2 Pg. 24
SGWB 50C 1	57.8898	1.1578	WIPP-pHCOR-2 Pg. 25
SGWB 50C 2*	57.8857	1.1577	WIPP-pHCOR-2 Pg. 25
SGWB 50C 3	57.8703	1.1574	WIPP-pHCOR-2 Pg. 25
	SGWB Density	1.1649	
	Standard Deviation	0.0104	

APPENDIX B: *pH correction factors*

Solution	A	Average	Standard Deviation	1σ	2σ	3σ
DGi-115SC electrode (fixed ground glass sleeve junction) 25 °C						
1 m NaCl 25C 1	0.076					
1 m NaCl 25C 2	0.089					
1 m NaCl 25C 3	0.087	0.084	0.007	0.001	0.001	0.002
2 m NaCl 25C 1	0.288					
2 m NaCl 25C 2	0.252					
2 m NaCl 25C 3	0.254	0.265	0.020	0.005	0.011	0.016
3 m NaCl 25C 1	0.428					
3 m NaCl 25C 2	0.416					
3 m NaCl 25C 3	0.430	0.425	0.008	0.003	0.006	0.010
4 m NaCl 25C 1	0.617					
4 m NaCl 25C 2	0.595					
4 m NaCl 25C 3	0.606	0.606	0.011	0.007	0.013	0.020
5 m NaCl 25C 1	0.757					
5 m NaCl 25C 2	0.763					
5 m NaCl 25C 3	0.786	0.769	0.015	0.012	0.024	0.035
WIPP-pHCOR-2 Pgs. 54-57						
Ross electrode (sure flow junction) 25 °C						
Solution	A	Average	Standard Deviation	**1σ**	**2σ**	**3σ**
1 m NaCl 25C 1	0.209					
1 m NaCl 25C 2	0.190					
1 m NaCl 25C 3	0.207	0.202	0.010	0.002	0.004	0.006
2 m NaCl 25C 1	0.378					
2 m NaCl 25C 2	0.421					
2 m NaCl 25C 3	0.427	0.408	0.027	0.011	0.022	0.033
3 m NaCl 25C 1	0.654					
3 m NaCl 25C 2	0.656					
3 m NaCl 25C 3	0.604	0.638	0.029	0.019	0.038	0.056
4 m NaCl 25C 1	0.791					
4 m NaCl 25C 2	0.799					
4 m NaCl 25C 3*	0.625	0.795	0.006	0.004	0.008	0.013
5 m NaCl 25C 1	0.988					
5 m NaCl 25C 2	0.969					
5 m NaCl 25C 3	1.039	0.999	0.036	0.036	0.072	0.108
WIPP-pHCOR-1 Pgs.48-52						
*Data is not consistent with other titrations and will not be used						
DGi-101SC electrode (ceramic frit junction) 25 °C						

Solution	A	Average	Standard Deviation	1σ	2σ	3σ
1 m NaCl 25C 1	-0.059					
1 m NaCl 25C 2	-0.073					
1 m NaCl 25C 3	-0.028	-0.054	0.023	-0.001	0.002	0.004
2 m NaCl 25C 1	0.138					
2 m NaCl 25C 2	0.144					
2 m NaCl 25C 3	0.141	0.141	0.003	0.000	0.001	0.001
3 m NaCl 25C 1	0.397					
3 m NaCl 25C 2	0.390					
3 m NaCl 25C 3	0.340	0.376	0.031	0.012	0.023	0.035
4 m NaCl 25C 1	0.508					
4 m NaCl 25C 2	0.527					
4 m NaCl 25C 3	0.543	0.526	0.018	0.009	0.019	0.028
5 m NaCl 25C 1	0.703					
5 m NaCl 25C 2	0.701					
5 m NaCl 25C 3	0.771	0.725	0.040	0.029	0.058	0.087
WIPP-pHCOR-1 Pgs. 93-96						

DGi-115SC (fixed ground-glass sleeve junction)

Solution	A	Average	Standard Deviation	1σ	2σ	3σ
SGWB 25C 1	0.856					
SGWB 25C 2	0.835					
SGWB 25C 3	0.745					
SGWB 25C 4	0.791	0.807	0.049	0.040	0.080	0.119
SGWB 30C 1	0.648					
SGWB 30C 2	0.632					
SGWB 30C 3	0.622	0.634	0.013	0.008	0.017	0.025
SGWB 40C 4	0.639					
SGWB 40C 5	0.553					
SGWB 40C 6	0.575					
SGWB 40C RR1	0.541					
SGWB 40C RR2	0.795	0.621	0.105	0.065	0.130	0.195
SGWB 50C 4	0.781					
SGWB 50C 5	0.809					
SGWB 50C 6	0.776	0.789	0.018	0.014	0.028	0.042
SGWB 60C 1	0.812					
SGWB 60C 2	0.830					
SGWB 60C 3	0.784	0.809	0.023	0.019	0.037	0.056
SGWB 70C 1	0.908					
SGWB 70C 2	0.871					
SGWB 70C 3	0.861	0.88	0.025	0.022	0.044	0.065
SGWB 80C 2	1.060					
SGWB 80C 3	1.001	1.03	0.042	0.043	0.086	0.129
WIPP-pHCOR-1 Pgs. 14-23 and 39-40						

Ross (sure flow junction)						
Solution	A	Average	Standard Deviation	**1σ**	**2σ**	**3σ**
SGWB 25C 1	0.926					
SGWB 25C 2	0.927					
SGWB 25C 3	0.893	0.915	0.019	0.018	0.035	0.053
SGWB 30C 1	0.779					
SGWB 30C 2	0.842					
SGWB 30C 3	0.819	0.813	0.032	0.026	0.052	0.078
SGWB 40C 4	0.940					
SGWB 40C 5	0.909					
SGWB 40C 6	0.893	0.914	0.024	0.022	0.044	0.066
SGWB 50C 4	0.905					
SGWB 50C 5	0.916					
SGWB 50C 6	0.954	0.925	0.026	0.024	0.048	0.071
SGWB 60C 1	0.974					
SGWB 60C 2	0.916					
SGWB 60C 3	0.953	0.948	0.029	0.028	0.056	0.083
SGWB 80C 1	1.046					
SGWB 80C 2	1.209					
SGWB 80C 3	0.817					
SGWB 80C 4	0.908	0.995	0.171	0.170	0.340	0.510
WIPP-pHCOR-2 Pgs. 24-35,38						
DGi-101SC (ceramic frit junction)				**1σ**	**2σ**	**3σ**
Solution	A	Average	Standard Deviation			
SGWB 25C 1	0.773					
SGWB 25C 2	0.837					
SGWB 25C 3	0.743	0.784	0.048	0.038	0.075	0.113
SGWB 30C 1*	0.609					
SGWB 30C 2	0.849					
SGWB 30C 3	0.853	0.851	0.003	0.002	0.005	0.007
SGWB 50C 1	0.803					
SGWB 50C 2*	0.639					
SGWB 50C 3	0.782	0.792	0.015	0.012	0.024	0.035
WIPP-pHCOR-2 Pgs. 24-25, 42						
*Data is not consistent with other analyses and will not be used in the calculation of the average or Std. Dev.						

APPENDIX C: *Equations for conversion from m to M and visa versa.*

$$m \times (m:M) = M$$

$$m:M = 1000\rho/[1000 + \Sigma(FW_{solute} \times m_{solute})]$$

where:

ρ	-density of solution in g/mL or kg/L
m_{solute}	-molality of a solute
FW_{solute}	-molecular weight of *i* species in g/mol

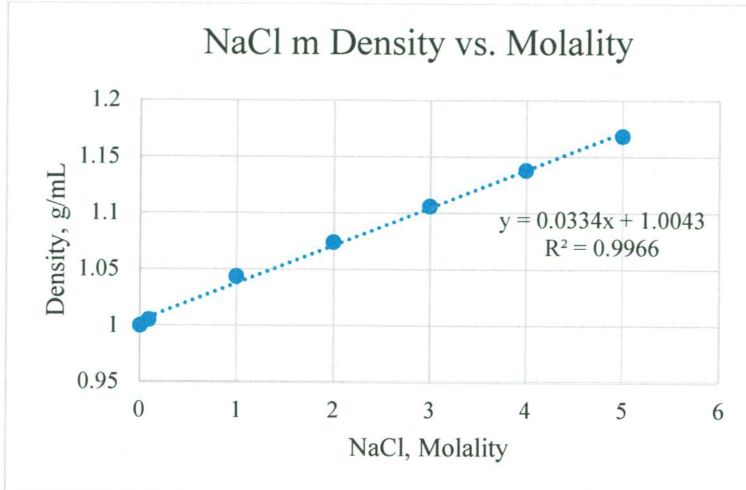
Starting Solutions from TP 18-01 and molal to Molarity calculations for all literature data

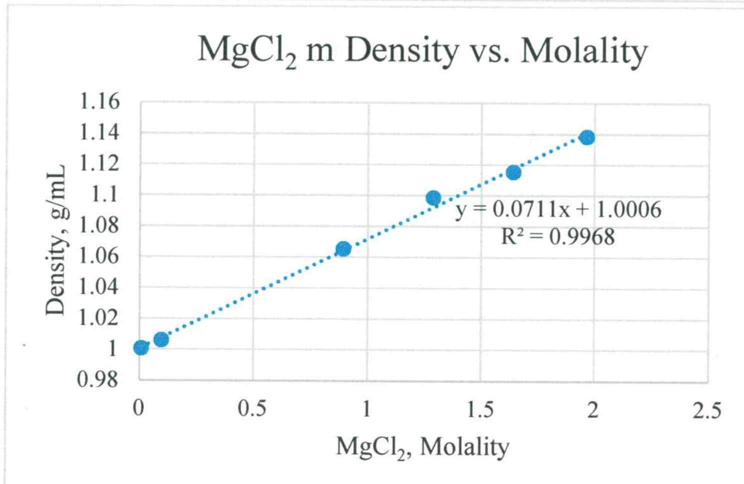
	NaCl, m	Density	NaCl, M
m to M conversions from TP18-01 Milestone Report, Appendix A, Section B and other literature data, using listed densities.	0.01	1.000	0.01
	0.10	1.005	0.10
	0.50	1.021	0.50
	1.00	1.044	0.99
	2.00	1.074	1.92
	3.00	1.106	2.82
	4.00	1.138	3.69
	5.00	1.168	4.52
	5.50	1.188	4.94
	5.60	1.191	5.03
	6.00	1.205	5.35

*0.5, 5.5, 5.6 and 6.0m densities calculated based on chart below

Solutions from Xiong, et al., 2010

	NaCl, m	NaCl, m Density calculation	NaCl, M	$MgCl_2$, m	$MgCl_2$ m Density Calculation	$MgCl_2$, M
Solution A	5.00	1.17	4.53	0.50	1.04	0.49
Solution B	3.50	1.12	3.26	0.80	1.06	0.79
Solution C	3.00	1.11	2.82	1.25	1.09	1.22
Solution D	2.00	1.07	1.92	1.50	1.11	1.45
Solution E	1.50	1.05	1.45	1.75	1.13	1.69
Solution F	0.50	1.02	0.50	2.00	1.14	1.92





$MgCl_2$ and NaCl figures are from the First Milestone Report for TP 18-01 (Kirkes, 2020)

APPENDIX D: *EQ3/6 Analysis of Solutions*

	EQ3/6 Analysis for listed brines							
	0.5m NaCl	1.0m NaCl	2.0m NaCl	3.0m NaCl	4.0m NaCl	5.0m NaCl	6.0m NaCl	SGWB
Temp (°C)	25	25	25	25	25	25	25	25
Pitzer pH	6.96	7.45	7.65	7.65	7.85	7.85	7.97	12.75
pH (NBS* scale)	6.95	7.43	7.60	7.55	7.70	7.64	7.71	12.63
pcH	6.86	7.40	7.74	7.88	8.23	8.39	8.68	13.06
a(w)	0.98354	0.96685	0.93155	0.89315	0.85152	0.80682	0.75944	0.86172
Log a(w)	-0.00721	-0.01464	-0.0308	-0.04907	-0.06981	-0.09322	-0.11951	-0.06463
Solution Density (g/mL)	1.0195	1.0376	1.0728	1.1066	1.1391	1.1703	1.2004	1.1484
Molality/Molarity (L/kg.H2O)	1.01E+00	1.02E+00	1.04E+00	1.06E+00	1.08E+00	1.10E+00	1.13E+00	1.09E+00
Na+ Molality	5.00E-01	1.00E+00	2.00E+00	3.00E+00	4.00E+00	5.00E+00	6.00E+00	3.10E+00
Mg++ Molality								1.27E-01
Cl- Molality	5.00E-01	1.00E+00	2.00E+00	3.00E+00	4.00E+00	5.00E+00	6.00E+00	4.01E+00
H+ Molality	1.39E-07	4.03E-08	1.91E-08	1.39E-08	6.39E-09	4.53E-09	2.37E-09	9.47E-14
MgOH+ Molality								7.83E-01
OH- Molality	1.39E-07	4.64E-07	7.63E-07	7.51E-07	1.12E-06	1.06E-06	1.33E-06	1.27E-01
A (pcH-pH NBS Scale)	-0.093	-0.030	0.136	0.327	0.531	0.744	0.963	0.427

Note*:EQ3/6 software package denotes pH on National Bureau of Standards (NBS) scale, however in 1988 the NBS became the National Institute of Standards and Technology (NIST)

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Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy.