SOFTWARE VALIDATION REPORT FOR

STREAMANALYZER VERSION 2.0

Prepared for

U.S. Nuclear Regulatory Commission
Contract NRC–02–02–012

Prepared by

Alka Jain
Roberto Pabalan
Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

November 2005

Approved by:

English Pearcy, Manager
Geochemistry

11/8/2005
Date

CONTENTS

Section Page

TABLES iv
ACKNOWLEDGMENTS v

1 SCOPE OF THE VALIDATION 1

2 SYSTEM REQUIREMENTS 1
2.1 Software 1
2.2 Hardware 1

3 PREREQUISITES 2

4 ASSUMPTIONS AND CONSTRAINTS 2

5 TEST CASES 2
5.1 Test Case 1—NaCl Solubility as a Function of Temperature 2
5.1.1 Test Input 2
5.1.2 Test Procedure 3
5.1.3 Test Results 3
5.2 Test Case 2—NaCl and KCl Solubility in Mixed NaCl+KCl Solutions 3
5.2.1 Test Input 3
5.2.2 Test Procedure 3
5.2.3 Test Results 4
5.3 Test Case 3—Solubility of $MgCl_2$ in $CaCl_2$-NaCl-KCl Solutions 4
5.3.1 Test Input 4
5.3.2 Test Procedure 4
5.3.3 Test Results 6
5.4 Test Case 4—Vapor Pressure of KCl Solutions at 300 °C [572 °F] as a Function of Concentration 7
5.4.1 Test Input 8
5.4.2 Test Procedure 8
5.4.3 Test Results 8
5.5 Test Case 5—Lowering of Vapor Pressure by $CaCl_2$ in Aqueous Solutions at 100 °C [212 °F] as a Function of Concentration 8
5.5.1 Test Input 8
5.5.2 Test Procedure 8
5.5.3 Test Results 8
5.6 Test Case 6—Lowering of Vapor Pressure by $NaNO_3$, NaOH, and $NaHSO_4$ in Aqueous Solutions at 100 °C [212 °F] 10
5.6.1 Test Input 10
5.6.2 Test Procedure 10
5.6.3 Test Results 10
5.7 Test Case 7—Deliquescence Point of Mixed NaCl-$NaNO_3$-KNO_3 Salts 10
5.7.1 Test Input 10
5.7.2 Test Procedure 10
5.7.3 Test Results 10

CONTENTS (continued)

Section Page

5.8 Test Case 8—Solubility of $NaNO_3$ and NaOH at Concentrations Beyond 30 m 11
5.8.1 Test Input 12
5.8.2 Test Procedure 12
5.8.3 Test Results 12

6 CONCLUSIONS 12

7 REFERENCES 13

APPENDIX—TEST CASE DATA FILES

TABLES

Table Page

1 Comparison of the Calculated NaCl Solubilities (S) with the Experimental Values 4

2 Comparison of Experimental and Calculated Solubility of NaCl and/or KCl in Mixed NaCl-KCl Solutions 5

3 Comparison of Experimental and Calculated Solubility of $MgCl_2$ in $CaCl_2$-KCl-NaCl Solutions 7

4 Comparison of Experimental and Calculated Vapor Pressure of KCl Solutions at 300 °C [572 °F] 9

5 Comparison of Experimental and Calculated Vapor Pressure of $CaCl_2$ Solutions at 100 °C [212 °F] 9

6 Comparison of Experimental and Calculated Vapor Pressure of $NaNO_3$, NaOH, and $NaHSO_4$ Solutions at 100 °C [212 °F] 11

7 Comparison of Experimental and Calculated Deliquescence Relative Humidity of $NaNO_3$-NaCl-KNO_3 Mixture at 86 °C [186.8 °F] 12

8 Comparison of the Calculated Solubilities (molal) with the Experimental Values for Concentrated $NaNO_3$ and NaOH Solutions 13

ACKNOWLEDGMENTS

This report was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC–02–02–012. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety. The report is an independent product of CNWRA and does not necessarily reflect the views or regulatory position of NRC.

The authors thank N. Naukam for her assistance in preparing this report. The authors also are grateful to L. Yang for technical discussions, and to J. McMurry, E. Hanson, and G. Wittmeyer for their reviews of the manuscript.

QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: No data were generated for this report.

ANALYSES AND CODES: This report documents quality assurance software validation activities for StreamAnalyzer Version 2.0. This software was developed by OLI Systems, Inc. Calculation results are documented in Electronic Scientific Notebook 716.

Reference

OLI Systems, Inc. *StreamAnalyzer*. Version 2.0. Morris Plains, New Jersey. 2005.

1 SCOPE OF THE VALIDATION

This report documents the validation of the simulation software StreamAnalyzer Version 2.0 based on the software validation test plan (Yang, 2002) and the test cases used in validating StreamAnalyzer Version 1.2 (Yang, 2003). The validation involved comparing calculated results with experimental data available in the literature.

StreamAnalyzer Version 2.0 is one of several software packages of the family of process simulation software developed by OLI Systems, Inc. These packages include Environmental Simulation Program (ESP), Corrosion Simulation Program (CSP), and StreamAnalyzer. ESP is used for evaluating the thermodynamic properties of different streams in a chemical process in industrial and environmental applications. CSP is used for evaluating the thermodynamic properties that are related to the characteristics of corrosion and the corrosion rate of a metal in a given solution system. A regular ESP/CSP package contains both the ESP and CSP components. StreamAnalyzer is essentially a component of the ESP and is packaged as a stand-alone software with a user-friendly graphic interface for evaluating the thermodynamic behavior of components of a single or of multiple aqueous streams. In contrast to previous versions of StreamAnalyzer Version 2.0 has a new chemistry model, referred to as the Mixed Solvent Electrolyte (MSE) model, and associated thermodynamic parameters. The standard chemistry model of StreamAnalyzer is applicable to aqueous systems with ionic strengths up to 30 molal. The new MSE model is capable of calculating speciation, chemical, and phase equilibria that are applicable to water-organic-salt systems in the full range of concentrations, as well as aqueous electrolytes from dilute solutions to the fused salt limit. Both chemistry models of StreamAnalyzer Version 2.0 were tested.

The scope of the validation was within the following ranges:

Temperature:	0 to 300 °C [0 to 572 °F]
Pressure:	0 to 1,480 atm [0 to 21,750 psi]
Ionic Strength:	0 to 30 molal for StreamAnalyzer Version 2.0 with the standard chemistry model; 0 to 130 molal for StreamAnalyzer Version 2.0 with the MSE chemistry model

2 SYSTEM REQUIREMENTS

2.1 Software

StreamAnalyzer Version 2.0 runs in a Microsoft® Windows environment (98, ME, NT, 2000, and XP). The validation test was conducted in Windows 2000.

2.2 Hardware

StreamAnalyzer Version 2.0 runs on the IBM [personal computer (PC)] family of microcomputers or compatible systems. According to the license agreement for PC users, the software can be installed on a network server, but a software key is required to permit one user at a time to run the software. The validation test was conducted with a Pentium III PC.

The input and output parameters can be printed to either a printer or a text spreadsheet file. StreamAnalyzer also supports graphical output to printers.

3 PREREQUISITES

Running the OLI simulation packages and compiling the results as a spreadsheet file requires spreadsheet software (e.g., Microsoft Excel® 97). The user of StreamAnalyzer must be familiar with chemical thermodynamics.

4 ASSUMPTIONS AND CONSTRAINTS

The standard chemistry model of StreamAnalyzer Version 2.0 is based on the standard-state properties using the Helgeson, et al. (1981) equation-of-state and excess properties using the aqueous activity coefficient expressions developed by Bromley (1972) and Pitzer (1991,1973). Using the standard chemistry model, StreamAnalyzer Version 2.0 has the following limitations:

Water Content:	> 65 percent (Molar basis)
Temperature:	−50 to 300 °C [−58 to 572 °F]
Ionic Strength:	0 to 30 molal
Pressure:	0 to 1,480 atm [0 to 21,750 psi]

The MSE chemistry model of StreamAnalyzer Version 2.0 is described in Wang, et al. (2002). It uses a Debye-Hückel equation on a mole-fraction basis to represent the long-range electrostatic interactions. Short-range interactions are represented by the UNIQUAC local composition model, and a Margules-type equation is used to represent the middle-range interactions. Using the MSE model, StreamAnalyzer Version 2.0 has the following limitations:

Water Content:	0 to 100 percent (Molar basis)
Temperature:	−50 to 300 °C [−58 to 572 °F]
Ionic Strength:	up to pure salts
Pressure:	0 to 1,480 atm [0 to 21,750 psi]

5 TEST CASES

The test cases described in this section involve calculations of mineral solubilities and vapor pressures of salt solutions and salt mixtures in the temperature range of 0 to 300 °C [32 to 572 °F].

5.1 Test Case 1—NaCl Solubility as a Function of Temperature

The solubility of NaCl(s) was calculated from 25 to 300 °C [77 to 572 °F] to verify whether StreamAnalyzer Version 2.0 can be used to accurately calculate the solubility of a single salt at different temperature conditions.

5.1.1 Test Input

Input temperatures were 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, and 300 °C [77, 122, 167, 212, 257, 302, 347, 392, 437, and 572 °F]. Below 100 °C [212 °F], the input pressure

was 1.0 atm [14.7 psi]. At 100 °C [212 °F] and above, the input pressure was the vapor saturation pressure at the temperature of interest.

5.1.2 Test Procedure

The test was run by specifying the calculation types as constant pressure at temperatures lower than 100 °C [212 °F] and bubble point at temperatures equal to or above 100 °C [212 °F].

5.1.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 (standard and MSE models) were saved to two files named StreamAnalyzer2.0AQU_Case1.xls and StreamAnalyzer2.0MSE_Case1.xls (see Appendix). These files list the temperatures and pressures used in the calculation, the resulting ionic strength, and the calculated concentrations of Na^+ and Cl^-. The calculated Na^+ (or Cl^-) concentrations were compared with experimental data given in Liu and Lindsay (1972) and Linke (1965), as shown in Table 1. The deviation (% Dev) of the test results from the experimental data are within ±10 percent and, therefore, are acceptable. The ±10 percent criterion is arbitrarily set in the validation test plan because ±10 percent variation in concentration would not significantly affect the estimated performance of the engineered barrier system in the repository system.

5.2 Test Case 2—NaCl and KCl Solubility in Mixed NaCl+KCl Solutions

The solubility of NaCl and KCl was calculated at different temperatures and compared with experimental data. The test was conducted to determine the ability of StreamAnalyzer Version 2.0 to accurately calculate the solubility of a mineral salt in a solution containing two types of dissolved salts and at different temperature conditions.

5.2.1 Test Input

Input temperatures were 40, 100, and 150 °C [104, 212, and 302 °F]. Below 100 °C [212 °F], the input pressure was 1.0 atm [14.7 psi]. At 100 °C [212 °F] and above, the input pressure was the vapor saturation pressure at the temperature of interest. When the solubility of NaCl was calculated, a fixed value of K^+ concentration and an extra amount of NaCl were specified in the input stream. On the other hand, when the solubility of KCl was calculated, a fixed value of Na^+ concentration and an extra amount of KCl were specified in the input stream. The solubilities of the two salts in the eutonic solution of NaCl and KCl were calculated by specifying extra amounts of both NaCl and KCl in the input stream.

5.2.2 Test Procedure

The test was run by specifying the calculation types as constant pressure at temperatures lower than 100 °C [212 °F] and bubble point at temperatures equal or above 100 °C [212 °F].

Table 1. Comparison of the Calculated NaCl Solubilities (S) with the Experimental Values													
Temperature °C*		**25**	**50**	**75**	**100**	**125**	**150**	**175**	**200**	**225**	**250**	**275**	**300**
Experimental†	S(m)	6.15	6.28	6.46	6.68	6.94	7.20	7.57	7.97	8.44	8.99	9.65	10.41
StreamAnalyzer Version 2.0 (MSE)	S(m)	6.13	6.27	6.48	6.72	6.97	7.24	7.52	7.83	8.35	8.94	9.67	10.42
	%Dev‡	−0.18	−0.03	0.33	0.60	0.55	0.52	−0.70	−1.84	−1.05	−0.51	0.21	0.04
StreamAnalyzer Version 2.0 (Standard)	S(m)	6.15	6.28	6.47	6.69	6.95	7.25	7.59	7.96	8.39	8.89	9.47	10.16
	%Dev‡	0.09	0.15	0.10	0.15	0.24	0.71	0.16	−0.12	−0.50	−1.14	−1.86	−2.41

* °F = (9/5) °C+32
†Compiled data are from Pabalan, R.T. "Software Validation Report for SOLCALC." Version 1.0. San Antonio, Texas: CNWRA. 2002; original data for T < 75 °C are from Linke, W.F. *Solubilities of Inorganic and Metal Organic Compounds*. Vols. 1 and 2. 4th Edition. Washington, DC: American Chemical Society. 1965. and Liu, C. and W.T. Lindsay. "Thermodynamics of Sodium Chloride Solutions at High Temperatures." *Journal of Solution Chemistry.* No. 1. pp. 45–69. 1972. for T > 75 °C.
‡% Dev—percent deviation

5.2.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 (standard and MSE models) were saved to two files named StreamAnalyzer2.0AQU_Case2.xls and StreamAnalyzer2.0MSE_Case2.xls (see Appendix). These files list the temperatures and pressures used in the calculation, the resulting ionic strength, and the calculated concentrations of Na^+, K^+, and Cl^-. The calculated Na^+, K^+, and Cl^- concentrations were compared with experimental data given in Linke (1965), as shown in Table 2. The deviations of the test results obtained with StreamAnalyzer Version 2.0 from the experimental data are within ±10 percent and, therefore, considered acceptable. The ±10 percent criterion is selected in the validation test plan because ±10 percent variation in concentration would not significantly affect the estimated performance of the engineered barrier system in the repository system.

5.3 Test Case 3—Solubility of $MgCl_2$ in $CaCl_2$-NaCl-KCl Solutions

The solubility of $MgCl_2$ in $CaCl_2$-NaCl-KCl solutions was calculated at 0 and 50 °C [32 and 122 °F] and compared with experimental data. The test was conducted to determine the ability of StreamAnalyzer Version 2.0 to accurately calculate the solubility of minerals in a solution containing multicomponent dissolved salts.

5.3.1 Test Input

The input temperature was 0 and 50 °C [32 and 122 °F], and the input pressure was 1.0 atm [14.7 psi]. The concentrations of Ca^{2+}, Na^+, and K^+ were varied, and the saturated concentration of Mg^{2+} was calculated with a slight excess of $MgCl_2$ in the solid phase.

5.3.2 Test Procedure

The test was run by specifying the calculation type as isothermal.

Table 2. Comparison of Experimental and Calculated Solubility of NaCl and/or KCl in Mixed NaCl-KCl Solutions

Solubility of NaCl in KCl Solutions

Temperature (°C)*	KCl Concentration (m)	Solubility of NaCl (m)				
		Measured†	StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyzer Version 2.0 (Standard)	
			Calculation	%Dev‡	Calculation	%Dev‡
40	0	6.217	6.207	−0.16	6.225	0.12
	0.87	5.801	5.767	−0.59	5.795	−0.11
	1.407	5.577	5.504	−1.30	5.540	−0.67
	1.733	5.409	—	—	5.389	−0.38
	2.566	5.12	4.961	−3.11	5.065	−1.07
100	0	6.68	6.720	0.61	6.690	0.15
	2.046	5.749	5.749	−0.01	5.694	−0.96
	4.024	4.791	—	—	4.856	1.36
	4.086	4.94	4.875	−1.31	4.832	−2.19
150	0	7.198	7.235	0.52	7.249	0.71
	4.024	5.698	5.609	−1.56	5.439	−4.55
	5.365	5.185	5.141	−0.85	4.953	−4.48

Solubility of KCl in NaCl Solutions

Temperature (°C)*	NaCl Concentration (m)	Solubility of KCl (m)				
		Measured†	StreamAnalyzer Version 2.0 (MSE)		StreamAnalyzer Version 2.0 (Standard)	
			Calculation	%Dev‡	Calculation	%Dev‡
40	0	5.37	5.428	1.08	5.416	0.85
	1.748	4.28	4.288	0.18	4.203	−1.79
	1.827	4.21	—	—	4.153	−1.35
	3.486	3.32	—	—	3.193	−3.83
	3.592	3.28	3.266	−0.43	3.138	−4.33
100	0	7.54	7.518	−0.29	7.491	−0.65
	1.717	6.44	6.414	−0.40	6.256	−2.85
	1.744	6.32	—	—	6.238	−1.30
	2.567	5.90	5.911	0.19	5.697	−3.44
	3.422	5.36	—	—	5.172	−3.50
	3.478	5.34	—	—	5.139	−3.76
	4.278	4.83	4.990	3.32	4.686	−2.98

Table 2. Comparison of Experimental and Calculated Solubility of NaCl and/or KCl in Mixed NaCl-KCl Solutions (continued)

Solubility of KCl in NaCl Solutions

	NaCl Concentration (m)	Solubility of KCl (m)				
		Measured†	StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyser Version 2.0 (Standard)	
			Calculation	%Dev‡	Calculation	%Dev‡
150	0	9.02	9.061	0.46	9.044	−0.27
	1.711	8.13	8.096	−0.42	7.831	−3.67
	2.567	7.64	7.650	0.14	7.274	−4.79
	3.422	7.15	—	—	6.752	−5.57
	4.278	6.71	6.832	1.82	6.266	−6.62

Solubility of NaCl and KCl in a NaCl-KCl Mixture

Calculation	T (°C)*	KCl Solubility (m)			NaCl Solubility (m)		
		Measured†	Calculation	%Dev‡	Measured†	Calculation	%Dev‡
Stream Analyzer Version 2.0 (MSE)	40	2.627	2.653	0.98	5.008	4.992	−1.73
	100	4.734	4.834	2.29	4.708	4.577	−2.79
	150	6.518	6.631	1.74	4.791	4.732	−1.23
Stream Analyzer Version 2.0 (Standard)	40	2.627	2.453	−6.61	5.008	5.065	1.14
	100	4.734	4.469	−5.60	4.708	4.685	−0.49
	150	6.518	6.021	−7.63	4.791	4.737	−1.14

* °F = (9/5) °C+32
†Data are from Pabalan, R.T. Software Validation Report for SOLCALC, Version 1.0. San Antonio, Texas: CNWRA. 2002; original data from Linke, W.F. *Solubilities of Inorganic and Metal Organic Compounds*. Vols. 1 and 2. 4th Edition. Washington, DC: American Chemical Society. 1965.
‡% Dev— percent deviation

5.3.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 (standard and MSE models) were saved to two files named StreamAnalyzer2.0AQU_Case3.xls and StreamAnalyzer2.0MSE_Case3.xls (see Appendix). These files list the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, and Cl^{-}. The calculated Mg^{2+} concentrations were compared with solubility data given by Korin and Roy (1988), as shown in Table 3. The deviations of the test results from the experimental data are within ±10 percent, except for one salt mixture composition at 50 °C [122 °F]. The differences

Table 3. Comparison of Experimental and Calculated Solubility of $MgCl_2$ in $CaCl_2$-KCl-NaCl Solutions

Temperature (°C)*	Fixed Salt Concentrations (m)			Solubility of $MgCl_2$ (m)				
					StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyzer Version 2.0 (Standard)	
	$CaCl_2$	KCl	NaCl	Measured†	Calculation	%Dev‡	Calculation	%Dev‡
50	0.000	0.021	0.050	6.457	6.195	−4.07	6.192	−4.11
	0.086	0.022	0.049	6.366	6.144	−3.49	6.144	−3.49
	0.182	0.022	0.050	6.279	6.090	−3.01	6.094	−2.95
	0.376	0.023	0.051	5.981	5.977	−0.06	5.989	0.13
	0.620	0.024	0.052	5.680	5.842	2.85	5.865	3.25
	0.768	0.025	0.051	5.391	5.762	6.86	5.792	7.44
	1.226	0.028	0.058	4.833	5.516	14.14	5.576	15.40
0	0.000	0.005	0.039	5.954	5.536	−7.02	5.547	−6.82
	0.127	0.005	0.040	5.754	5.437	−5.51	5.459	−5.14
	0.274	0.005	0.040	5.519	5.323	−3.55	5.357	−2.93
	0.538	0.005	0.042	5.175	5.116	−1.12	5.176	0.02
	0.880	0.006	0.041	4.697	4.850	3.25	4.946	5.31
	1.042	0.006	0.044	4.546	4.722	3.88	4.838	6.44
	1.146	0.007	0.048	4.401	4.640	5.43	4.769	8.36

* °F = (9/5) °C+32
†Korin, E.J. and A.S. Roy. "Heterogeneous Equilibrium in the Quinary System NaCl-KCl-$MgCl_2$-$CaCl_2$-H_2O in 0–50 °C Temperature Range." *Journal of Chemical Engineering Data*. Vol. 33. pp. 60–64. 1988.
‡% Dev—percent deviation

between the experimental value and the values calculated using StreamAnalyzer Version 2.0 using the MSE and standard chemistry models are 12.2 and 15.2 percent, respectively. Although these differences are higher than the ±10-percent criterion set in the validation test plan, the experimental uncertainties likely are higher for multicomponent $Ca^{2+}/Na^{+}/K^{+}/Mg^{2+}/Cl^{-}$ salt mixtures compared to single or binary salt mixtures. Thus, the validation results of StreamAnalyzer Version 2.0 for Test Case 3 are considered acceptable.

5.4 Test Case 4—Vapor Pressure of KCl Solutions at 300 °C [572 °F] as a Function of Concentration

The vapor pressure of KCl solutions as a function of concentration was calculated and compared with experimental data. The test was conducted to determine the ability of StreamAnalyzer Version 2.0 to accurately calculate the vapor pressures of single alkaline-chloride solutions.

5.4.1 Test Input

The input temperature was 300 °C [572 °F], and the input pressure was the vapor saturation pressure at the temperature of interest. The input KCl concentrations were varied.

5.4.2 Test Procedure

The test was run by specifying the calculation type as bubble point.

5.4.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 and StreamAnalyzer Version 2.0 MSE were saved to two files named StreamAnalyzer2.0AQU_Case4.xls and StreamAnalyzer2.0MSE_Case4.xls (see Appendix). These files list the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of K^+ and Cl^-. The calculated KCl solution vapor pressure was compared with vapor pressure data from Zarembo, et al. (1976), as shown in Table 4. The test results are considered acceptable because they are within ±10 percent of experimental data.

5.5 Test Case 5—Lowering of Vapor Pressure by $CaCl_2$ in Aqueous Solutions at 100 °C [212 °F] as a Function of Concentration

The vapor pressures of $CaCl_2$ solutions as functions of concentration were calculated and compared with experimental data. The test was conducted to determine the ability of StreamAnalyzer Version 2.0 to accurately calculate the vapor pressures of alkaline-earth-metal chloride solutions.

5.5.1 Test Input

The input temperature was 100 °C [212 °F], and the input pressure was the vapor saturation pressure. The input $CaCl_2$ concentrations were varied.

5.5.2 Test Procedure

The test was run by specifying the calculation type as bubble point.

5.5.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 (standard and MSE models) were saved to two files named StreamAnalyzer2.0AQU_Case5.xls and StreamAnalyzer2.0MSE_Case5.xls (see Appendix). These files list the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of Ca^{2+} and Cl^-. The calculated $CaCl_2$ solution vapor pressure was compared with handbook vapor pressure data, as shown in Table 5. The deviations of the test results from the experimental data are within ±10 percent and, therefore, considered acceptable.

Table 4. Comparison of Experimental and Calculated Vapor Pressure of KCl Solutions at 300 °C [572 °F]					
	Vapor Pressure (Bar)				
		StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyzer Version 2.0 (Standard)	
KCl Concentration (m)	Measured*	Calculation	%Dev†	Calculation	%Dev†
0.549	85.70	80.03	−6.62	81.36	−5.06
0.966	84.78	78.93	−6.90	80.28	−5.31
1.392	83.32	77.93	−6.47	79.21	−4.93
1.904	81.78	76.73	−6.18	77.97	−4.66
2.954	79.02	74.36	−5.89	75.64	−4.28
3.388	77.62	73.41	−5.43	74.75	−3.70
4.283	75.26	71.45	−5.07	73.04	−2.95
4.528	74.56	70.91	−4.96	72.61	−2.62

*Data are from Pabalan, R.T. "Software Validation Report for SOLCALC." Version 1.0. San Antonio, Texas: CNWRA. 2002; original data are from Zarembo, V.I., N.A. Antonov, V.N. Gilyarov, and M.K. Fedorov. "Activity Coefficients of KCl in the System KCl-H_2O at Temperatures of 150–350 °C and Pressures up to 1500 kg/cm^2." *Journal of Applied Chemistry*. Vol. 49. pp. 1,259–1,263. 1976.
†% Dev—percent deviation

Table 5. Comparison of Experimental and Calculated Vapor Pressure of $CaCl_2$ Solutions at 100 °C [212 °F]					
	Vapor Pressure (atm)				
		StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyzer Version 2.0 (Standard)	
$CaCl_2$ Concentration (m)	Measured*	Calculation	%Dev†	Calculation	%Dev†
0.5	0.978	0.975	−0.23	0.974	−0.33
1	0.948	0.947	−0.02	0.946	−0.14
2	0.875	0.873	−0.24	0.871	−0.37
3	0.781	0.778	−0.30	0.776	−0.56
4	0.682	0.676	−0.96	0.672	−1.57
5	0.580	0.576	−0.63	0.569	−1.91

*Lide, D.R., ed. *CRC Handbook of Chemistry and Physics.* 77th Edition. Boston, Massachusetts: CRC Press. 1997.
†% Dev—percent deviation

5.6 Test Case 6—Lowering of Vapor Pressure by $NaNO_3$, NaOH, and $NaHSO_4$ in Aqueous Solutions at 100 °C [212 °F]

5.6.1 Test Input

The input temperature was 100 °C [212 °F], and the input pressure was the vapor saturation pressure. The input concentrations of $NaNO_3$, NaOH, and $NaHSO_4$ were varied.

5.6.2 Test Procedure

The test was run by specifying the calculation type as bubble point.

5.6.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 (standard and MSE models) were saved to two files named StreamAnalyzer2.0AQU_Case6.xls and StreamAnalyzer2.0MSE_Case6.xls (see Appendix). These files list the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of cations and anions. The calculated solution vapor pressures were compared with handbook vapor pressure data, as shown in Table 6. The deviations of the test results from the experimental data are within ±10 percent, except for one case where the standard chemistry model of StreamAnalyzer Version 2.0 was applied to an aqueous solution with a high concentration (10 molal) of $NaHSO_4$. The deviation in this case is −10.4 percent, slightly higher than the ±10-percent criterion set in the test plan. The validation results of StreamAnalyzer Version 2.0 for Test Case 6 are considered acceptable, but caution is advised when applying the standard chemistry model of StreamAnalyzer Version 2.0 for aqueous solutions containing high concentrations of $NaHSO_4$.

5.7 Test Case 7—Deliquescence Point of Mixed NaCl-$NaNO_3$-KNO_3 Salts

The mutual deliquescence point of mixed NaCl-$NaNO_3$-KNO_3 salts was calculated and compared with experimental data. The test was conducted to determine the ability of StreamAnalyzer 2.0 to accurately calculate the mutual deliquescence point of mixed salts.

5.7.1 Test Input

The input temperature was 86 °C [186.8 °F]. The input concentrations of $NaNO_3$, NaCl, and KNO_3 were specified such that undissolved $NaNO_3$, NaCl, and KNO_3 were present in the output streams.

5.7.2 Test Procedure

The test was run by specifying the calculation type as bubble point.

5.7.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 (standard and MSE models) were saved to two files named StreamAnalyzer2.0AQU_Case7.xls and StreamAnalyzer2.0MSE_Case7.xls (see Appendix). These files list the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of Na^+, NO_3^-, Cl^-, and K^+. The

Table 6. Comparison of Experimental and Calculated Vapor Pressure of $NaNO_3$, NaOH, and $NaHSO_4$ Solutions at 100 °C [212 °F]					
	Vapor Pressure of $NaNO_3$ Solution (atm)				
		StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyzer Version 2.0 (Standard)	
$NaNO_3$ Concentration (m)	Measured*	Calculation	%Dev†	Calculation	%Dev†
2	0.939	0.935	−0.50	0.938	−0.15
4	0.881	0.877	−0.49	0.879	−0.21
6	0.827	0.825	−0.25	0.825	−0.20
8	0.779	0.777	−0.31	0.775	−0.49
10	0.738	0.733	−0.78	0.730	−1.13
	Vapor Pressure of NaOH Solution (atm)				
		StreamAnalyzer Version 2.0 (MSE)		StreamAnalyzer Version 2.0 (Standard)	
NaOH Concentration (m)	Measured*	Calculation	%Dev†	Calculation	%Dev†
2	0.937	0.927	−1.07	0.930	−0.65
4	0.859	0.844	−1.72	0.854	−0.53
6	0.773	0.755	−2.27	0.771	−0.24
8	0.680	0.668	−1.80	0.686	0.94
10	0.587	0.585	−0.38	0.603	2.70
	Vapor Pressure of $NaHSO_4$ Solution (atm)				
		StreamAnalyzer Version 2.0 (MSE)		StreamAnalyzer Version 2.0 (Standard)	
$NaHSO_4$ Concentration (m)	Measured*	Calculation	%Dev†	Calculation	%Dev†
2	0.938	0.927	−1.17	0.929	−0.92
4	0.868	0.858	−1.14	0.848	−2.32
6	0.805	0.797	−0.98	0.762	−5.35
8	0.750	0.743	−0.93	0.688	−8.25
10	0.696	0.695	−0.15	0.623	−10.40

*Lide, D.R., ed. *CRC Handbook of Chemistry and Physics*. 77th Edition. Boston, Massachusetts: CRC Press. 1997.
†% Dev—percent deviation

calculated deliquescence point is the ratio of the vapor pressure of an aqueous solution saturated with the three salts and the vapor pressure of pure water. The calculated values were compared with the deliquescence point measured in the experiments (Yang, et al., 2002), as shown in Table 7. The deviations of the test result obtained with the StreamAnalyzer Version 2.0 (standard and MSE chemistry models) from the experimental data are within ±10 percent and, therefore, considered acceptable.

5.8 Test Case 8—Solubility of $NaNO_3$ and NaOH at Concentrations Beyond 30 M

The solubilities of $NaNO_3$ and NaOH salts were calculated and compared with experimental data. The test was conducted to determine the ability of the StreamAnalyzer Version 2.0 software using the MSE chemistry model to accurately calculate the solution properties of extremely concentrated aqueous solutions.

Table 7. Comparison of Experimental and Calculated Deliquescence Relative Humidity of $NaNO_3$-NaCl-KNO_3 Mixture at 86 °C [186.8 °F]				
Deliquescence Relative Humidity of $NaNO_3$-NaCl-KNO_3 Saturated Solution (%)				
	StreamAnalyzer Version 2.0 Mixed Solvent Electrolyte (MSE)		StreamAnalyzer Version 2.0 (Standard)	
Measured*	Calculation	%Dev†	Calculation	%Dev†
43.4	44.0	1.3	43.8	0.8

*Yang, L., R.T. Pabalan, and L. Browning. "Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multi-Component Salt Mixtures." Scientific Basis for Nuclear Waste Management XXV. Symposium Proceedings Vol. 713. Boston, Massachusetts: Materials Research Society. pp. 135–142. 2002.
†%Dev—deviation

5.8.1 Test Input

The input temperature used was from 94 to 202 °C [201.2 to 395.6 °F]. The input concentrations of $NaNO_3$ and NaOH were specified such that undissolved $NaNO_3$ and NaOH were present in the output streams.

5.8.2 Test Procedure

The test was run by specifying the calculation type either as a bubble point or precipitation point.

5.8.3 Test Results

The results of calculations with StreamAnalyzer Version 2.0 with option MSE were saved to StreamAnalyzer2.0MSE_Case8.xls (see Appendix). The file lists the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of Na^+, NO_3^-, and OH^-. The calculated solubility values were compared with the published solubility data (Linke, 1965), as shown in Table 8. The deviations of the test results from the experimental data are within ±10 percent, with the exception of the NaOH value at 192 °C [378 °F], which had a deviation of 18.1 percent. Although the deviation is higher than the ±10-percent criterion set in the validation test plan, the validation results nevertheless are considered acceptable because the experimental error at the high temperature {192 °C [378 °F]} and concentration (130.3 molal) of the solution with the 18.1-percent deviation is expected to be much higher than for solutions at lower temperatures and lower concentrations.

6 CONCLUSIONS

StreamAnalyzer Version 2.0, with the standard and MSE chemistry models, was tested in the following cases:

(1) Solubility of a single salt (NaCl) in the temperature range from 25 to 300 °C [77 to 572 °F]

(2) Solubility of binary salts (NaCl and KCl) in the temperature range from 40 to 150 °C [104 to 302 °F]

Table 8. Comparison of the Calculated Solubilities (molal) with the Experimental Values for Concentrated $NaNO_3$ and NaOH Solutions									
Salt	**Temperature (°C)***	**94.05**	**106.8**	**114.9**	**136.9**	**151.6**	**178**	**183.8**	**201.6**
$NaNO_3$	Expt†	19.5	21.9	23.5	28.9	33.6	44.6	47.8	59.8
	Calc.	19.2	21.4	23.0	28.6	33.6	46.4	50.2	60.0
	%Dev‡	−1.74	−2.10	−2.17	−1.00	−0.12	4.17	5.13	0.27
NaOH	**Temperature (°C)***	**30**	**40**	**50**	**60**	**80**	**110**	**192**	**—**
	Expt†	29.8	32.3	36.3	43.5	78.3	91.3	130.3	—
	Calc.	29.4	32.1	36.0	41.2	77.1	90.9	153.8	—
	%Dev‡	−1.34	−0.43	−0.61	−0.74	−1.42	−0.35	18.1	—

* °F = (9/5) °C+32
† Linke, W.F. *Solubilities of Inorganic and Metal Organic Compounds*. Vols. 1 and 2. 4th Edition. Washington, DC: American Chemical Society. 1965.
‡%Dev—percent deviation

(3) Solubility of $MgCl_2$ in $CaCl_2$-NaCl-KCl Solutions at 0 to 50 °C [32 to 122 °F]

(4) Vapor pressure of an alkaline chloride (KCl) solution at 300 °C [572 °F] at concentrations up to 4.5 m

(5) Lowering of vapor pressure by an alkaline-earth-metal chloride ($CaCl_2$) in an aqueous solution at 100 °C [212 °F] at concentrations up to 5 molal

(6) Lowering of vapor pressure by a nitrate ($NaNO_3$), a hydroxide (NaOH) and a bisulphate ($NaHSO_4$) in aqueous solutions at 100 °C [212 °F]

(7) Mutual deliquescence point of a multi-component salt mixture (NaCl-$NaNO_3$-KNO_3)

(8) Solubility of a salt ($NaNO_3$) and a hydroxide (NaOH) at concentrations beyond 30 molal (StreamAnalyzer Version 2.0 using the MSE chemistry model only)

The results obtained with StreamAnalyzer Version 2.0 are acceptable for all cases and can be used subject to the limits listed in Section 4.

7 REFERENCES

Bromley, L.A. "Approximate Individual Ion Values of β (or B) in Extended Debye-Huckel Theory for Uni-Univalent Aqueous Solutions at 298.15 K." *Journal of Chemical Thermodynamics*. Vol. 4. p. 669. 1972.

Helgeson, H.C., D.H. Kirkham, and G.C. Flowers. "Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures IV Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600 °C and 5 kb." *American Journal of Science*. Vol. 281. p. 1,249. 1981.

Korin, E.J. and A.S. Roy. "Heterogeneous Equilibrium in the Quinary System NaCl-KCl-$MgCl_2$-$CaCl_2$-H_2O in 0–50 °C Temperature Range." *Journal of Chemical Engineering Data*. Vol. 33. pp. 60–64. 1988.

Linke, W.F. *Solubilities of Inorganic and Metal Organic Compounds*. Vols. 1 and 2. 4th Edition. Washington, DC: American Chemical Society. 1965.

Liu, C. and W.T. Lindsay. "Thermodynamics of Sodium Chloride Solutions at High Temperatures." *Journal of Solution Chemistry.* No. 1. pp. 45–69. 1972.

Pitzer, K.S., ed. *Activity Coefficients in Electrolyte Solutions*. 2nd Edition. Boston, Massachusetts: Chemical Rubber Company, CRC Press. pp. 75–153. 1991.

Pitzer, K.S. "Thermodynamics of Electrolytes 1: Theoretical Basis and General Equations." *Journal of Physics and Chemistry*. Vol. 77. pp. 268–277. 1973.

Wang, P., A. Anderko, and R.D. Young. "A Speciation-Based Model for Mixed-Solvent Electrolyte Systems." *Fluid Phase Equilibria*. Vol. 203. pp. 141–176. 2002.

Yang, L. "Software Validation Report for Environmental Simulation Program (ESP), Version 6.6, Corrosion Simulation Program (CSP) Version 2.3, Environmental Simulation Program for Concentrated Brines (ESPCB) Version 7.0 Alfa, and Streamanalyzer Version 1.2." San Antonio, Texas: CNWRA. 2003.

———. "Software Validation Test Plan for Environmental Simulation Program (ESP) Version 6.5/Corrosion Simulation Program (CSP) Version 2.2, Environmental Simulation Program for Concentrated Brine Solutions (ESPCB) Version 7.0 Alfa and StreamAnalyzer 1.1." San Antonio, Texas: CNWRA. 2002.

Yang, L., R.T. Pabalan, and L. Browning. "Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multi-Component Salt Mixtures." Scientific Basis for Nuclear Waste Management XXV. Symposium Proceedings Vol. 713. Boston, Massachusetts: Materials Research Society. pp. 135–142. 2002.

Zarembo, V.I., N.A. Antonov, V.N. Gilyarov, and M.K. Fedorov. "Activity Coefficients of KCl in the System KCl-H_2O at Temperatures of 150–350 °C and Pressures up to 1500 kg/cm^2." *Journal of Applied Chemistry*. Vol. 49. pp. 1,259–1,263. 1976.

APPENDIX

TEST CASE DATA FILES

The following data files are in the CD enclosed with this report:

Test Results from StreamAnalyzer 2.0 using the MSE chemistry model

StreamAnalyzer2.0MSE_Case1.xls
StreamAnalyzer2.0MSE_Case2.xls
StreamAnalyzer2.0MSE_Case3.xls
StreamAnalyzer2.0MSE_Case4.xls
StreamAnalyzer2.0MSE_Case5.xls
StreamAnalyzer2.0MSE_Case6.xls
StreamAnalyzer2.0MSE_Case7.xls
StreamAnalyzer2.0MSE_Case8.xls

Test Results from StreamAnalyzer 2.0 using the standard chemistry model

StreamAnalyzer2.0AQU_Case1.xls
StreamAnalyzer2.0AQU_Case2.xls
StreamAnalyzer2.0AQU_Case3.xls
StreamAnalyzer2.0AQU_Case4.xls
StreamAnalyzer2.0AQU_Case5.xls
StreamAnalyzer2.0AQU_Case6.xls
StreamAnalyzer2.0AQU_Case7.xls