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 1.2

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Prepared by

Lietai Yang
Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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Approved by:

Vijay Jain, Element Manager
Corrosion Science and Process Engineering

Date 12/19/03

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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 ESP 6.6/CSP2.3, StreamAnalyzer1.2, and ESPCB 7.0. These software packages were developed by OLI systems. Calculation results are documented in Scientific Notebook 572.

1 SCOPE OF THE VALIDATION

This report documents the validation of the following OLI simulation software packages: Environmental Simulation Program (ESP) Version 6.6/Corrosion Simulation Program (CSP) 2.3, StreamAnalyser 1.2 and Environmental Simulation Program for Concentrated Brines (ESPCB) Version 7.0, as described in the software validation test plan (Yang, 2002). These software packages are the recent versions of the simulation programs. The validation test plan was for earlier versions of the software packages that were available at the time the plan was prepared. Because there are no significant difference between the newer and the older versions of these software packages, the test plan for the older versions of the package was used to validate these newer versions. The validation involved comparing calculated results with experimental data available in the literature.

ESP/CSP, StreamAnalyzer, and ESPCB are different packages of the simulation family developed by OLI Systems, Inc. (Morris Plains, New Jersey). ESP is for evaluating the thermodynamic properties of different streams in a chemical process in industrial and environmental applications. ESP has a large database of thermodynamic parameters and represents standard-state properties using the Helgeson-Kirkham-Flowers (1981) equation-of-state and excess properties using the aqueous activity coefficient expressions developed by Bromley (1972) and Pitzer (1973, 1991). These models enable simulation of aqueous chemical systems using ESP for temperatures to 300 °C [572 °F], pressures to 1,500 atm [2,204 psi], and ionic strengths up to 30 molal. CSP is 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 packaged as a stand-alone software for evaluating the thermodynamic behavior of components of a single aqueous stream. StreamAnalyzer has been added with a user-friendly graphic interface. ESPCB is a special version of ESP specifically developed for Southwest Research Institute®, which contains an additional Mixed Solvent Electrolyte Model and some additional new data. ESPCB is suitable for use in highly concentrated salts (close to or above 30 molal).

The scope of the validation was within the following ranges:

Temperature:	0 to 300 °C [0–572 °F]
Pressure:	0 to 1500 atm (saturation pressure of water) [0–2204 psi]
Ionic Strength:	0 to 30 molal for the ESP 6.6, CSP 2.3 and StreamAnalyzer 1.2
	0 to 50 molal for ESPCB 7.0 Alfa

The validation for CSP is limited to stability diagram calculation. The calculation for corrosion rate is not part of this validation.

2 SYSTEM REQUIREMENTS

2.1 Software

The family of the OLI simulation packages ESP Version 6.6/CSP Version 2.3, StreamAnalyser Version 1.2, and ESPCB Version 7.0 Alfa run in a Windows environment (95, 98, 2000, Me and NT). The validation test was conducted in Windows 2000.

2.2 Hardware

The family of the OLI simulation packages ESP Version 6.6/CSP Version 2.3, StreamAnalyzer Version 1.2, and ESPCB Version 7.0 Alfa run on the IBM PC family of microcomputers or compatible systems. According to the license agreement for PC users, the software can be installed on many computers. However, a hardware key is required on the microcomputer that runs the program. With only one hardware key issued to a license holder, only one user is allowed to use the software at a given time. The family of the OLI simulation packages can also run on a network. With a network license, the program can be run by users at different computers on the network. However, only one user is allowed to use the software at any given time. 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. The CSP and StreamAnalyzer also support graphical output to printers.

3 PREREQUISITES

Running the OLI simulation packages and compiling the results as a spreadsheet file requires spreadsheet software, such as MS Excel 97.

4 ASSUMPTIONS AND CONSTRAINTS

The user of OLI packages is assumed to be familiar with chemical thermodynamics.

The ESP 6.6/CSP2.3 and StreamAnalyser 1.2 are based on the standard-state properties using the Helgeson-Kirkham-Flowers (1981) equation-of-state and excess properties using the aqueous activity coefficient expressions developed by Bromley (1972) and Pitzer (1973,1991). The software has the following limitations:

Water content:	> 65 percent (Molar basis)
Temperature:	-50 to 300 °C [-122 to 572 °F]
Ionic Strength:	0 to 30 molal
Pressure:	0 to 1500 atm [0 to 2,204 psi]

The limitations for the ESPCB 7.0 Alfa are:

Water content:	up to 100 percent (Molar basis)
Temperature:	-50 to 300 °C [-122 to 572 °F]
Ionic Strength:	up to fused salts
Pressure:	0 to 1,500 atm [0 to 2,204 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 if the ESP6.6/CSP2.3, StreamAnalyzer 1.2, and ESPCB 7.0 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. Below 100 °C [77, 122, 167, 212, 257, 302, 347, 392, 437 and 572 °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 or above 100 °C [212 °F].

5.1.3 Test Results

The results of calculations with ESP6.6/CSP2.3, StreamAnalyser1.2 and ESPCB7.0 Alfa were saved to three files named ESP_Case1.xls, StreamAnalyser_Case1.xls, and EXPCB_Case1.xls, respectively (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/or KCl Solubility in Mixed NaCl+KCl Solutions

The solubility of NaCl and/or KCl was calculated at different temperatures and compared with experimental data. The test was to determine the ability of the OLI software 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 was 40, 100, and 150 °C [104, 212, and 302 °F]. Below 100 °C [212 °F], the input pressure was1.0 atm [14.7 psi]. At 100 °C [212 °F] and above, the input pressure was the

Table 1. Comparison of the Calculated NaCl Solubilities with the Experimental Values													
Temp °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
ESP Calc.	S(m)	6.15	6.28	6.47	6.69	6.95	7.25	7.58	7.96	8.39	8.89	9.46	10.16
	%Dev	0.09	0.15	0.10	0.15	0.24	0.71	0.16	-0.12	-0.50	-1.14	-1.91	-2.41
ESPCB Calc.	S(m)	6.14	6.26	6.47	6.73	7.01	7.27	7.62	7.98	8.35	8.78	9.33	10.22
	%Dev	-0.05	-0.25	0.12	0.76	1.07	1.05	0.61	0.04	-0.97	-2.33	-3.31	-1.86
S.A. Calc.	S(m)	6.15	6.28	6.47	6.69	6.95	7.25	7.58	7.96	8.39	8.89	9.46	10.16
	%Dev	0.09	0.15	0.10	0.15	0.24	0.71	0.16	-0.12	-0.50	-1.14	-1.91	-2.41

*Compiled data are from Pabalan, 2002; original data are from Linke, 1965; for T<75 °C and Liu and Lindsay, 1972 for T>75 °C.

References:

Linke, W.F. *Solubilities of Inorganic and Metal Organic Compounds.* Vols. 1 and 2. 4th Edition. Washington, DC: American Chemical Society. p. 1,070. 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.

Pabalan, R.T. "Software Validation Report for Solcalc, Version 1.0." San Antonio, Texas: CNWRA. 2002.

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].

5.2.3 Test Results

The results of calculations with ESP6.6/CSP2.3, StreamAnalyser1.2, and ESPCB7.0 Alfa were saved to three files named ESP_Case2.xls, StreamAnalyser_Case2.xls, and EXPCB_Case2.xls, respectively (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^+, (or Cl^-) concentrations were compared with experimental data given in Linke (1965), as shown in Table 2. The deviations of the test results obtained with the ESP 6.6 and StreamAnalyzer 1.2 from the experimental data are within ±10 percent and, therefore, considered acceptable for ESP 6.6 and StreamAnalyzer 1.2. 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. However, the deviation for ESPCB are beyond the ±10 percent target even at 40 °C [104 °F]. Therefore, ESPCB is not acceptable for solubility calculations with the NaCl-KCl-H_2O system. The vendor acknowledges that there was a

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

T (°C)	mKCl (m)	Solubility of NaCl (m)						
			ESP		ESPCB		StreamAnalyzer	
		Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
40	0	6.217	6.225	0.121	6.204	-0.208	6.225	0.121
	0.87	5.801	5.795	-0.109	—	—	5.795	-0.109
	1.407	5.577	5.540	-0.671	5.399	-3.192	5.540	-0.671
	1.733	5.409	5.389	-0.378	—	—	5.389	-0.377
	2.566	5.12	5.016	-2.031	4.897	-4.363	5.016	-2.031
100	0	6.68	6.690	0.153	6.731	0.770	6.690	0.153
	2.046	5.749	5.694	-0.957	5.562	-3.247	5.694	-0.957
	4.024	4.791	4.856	1.360	—	—	4.856	1.361
	4.086	4.94	4.832	-2.188	4.496	-8.994	4.832	-2.188
150	0	7.198	7.249	0.711	7.275	1.063	7.249	0.711
	4.024	5.698	5.439	-4.545	5.094	-10.592	5.439	-4.545
	5.365	5.185	4.953	-4.476	4.445	-14.275	4.953	-4.476

Solubility of KCl in NaCl Solutions

T (°C)	mNaCl (m)	Solubility of KCl (m)						
			ESP		ESPCB		StreamAnalyzer	
		Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
40	0	5.37	5.603	4.333	5.363	-0.123	5.603	4.333
	1.748	4.28	4.373	2.167	4.119	-3.764	4.373	2.168
	1.827	4.21	4.322	2.651	—	—	4.322	2.652
	3.486	3.32	3.342	0.660	—	—	3.342	0.659
	3.592	3.28	3.286	0.170	2.992	-8.773	3.286	0.171
100	0	7.54	7.688	1.958	7.530	-0.131	7.688	1.959
	1.717	6.44	6.440	0.000	—	—	6.440	0.001
	1.744	6.32	6.421	1.606	—	—	6.422	1.607
	2.567	5.90	5.874	-0.437	5.552	-5.899	5.874	-0.435

Table 2. Comparison of Experimental and Calculated Solubility of NaCl and/or KCl in Mixed NaCl-KCl Solutions (continued)								
150	0	9.02	9.382	4.008	9.114	-9.092	9.382	4.009
	1.711	8.13	8.156	0.317	—	1.041	8.156	0.318
	2.567	7.64	7.592	-0.634	7.094	—	7.592	-0.634
	3.422	7.15	7.063	-1.218	—	-7.150	7.063	-1.218
	4.278	6.71	6.570	-2.087	5.943	-11.429	6.570	-2.087

Solubility of NaCl and KCl in a NaCl-KCl Mixture							
		KCl Solubility (m)			NaCl Solubility (m)		
Calculation	T (°C)	Measured*	Calc.	%Dev	Measured*	Calc.	%Dev
ESP	40	2.627	2.611	-0.601	5.008	4.996	-0.232
	100	4.734	4.668	-1.398	4.708	4.610	-2.075
	150	6.518	6.381	-2.096	4.791	4.624	-3.491
ESPCB	40	2.627	2.325	-11.501	5.008	4.897	-2.224
	100	4.734	4.338	-8.355	4.708	4.361	-7.380
	150	6.518	5.943	-8.820	4.791	4.178	-12.788
Stream Analyzer	40	2.627	2.611	-0.602	5.008	4.996	-0.232
	100	4.734	4.668	-1.397	4.708	4.610	-2.075
	150	6.518	6.381	-2.095	4.791	4.624	-3.492

*Data are from Pabalan, 2002; original data from Linke, 1965.

References:

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

Pabalan, R.T. "Software Validation Report for Solcalc, Version 1.0." San Antonio, Texas: CNWRA. 2002.

problem with their data bank for some mixed salts for ESPCB 7.0 and claimed that the problem with the NaCl-KCl system has been resolved for their future release of the software.

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 to determine the ability of the OLI packages 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.

5.3.3 Test Results

The results of calculations with ESP6.6/CSP2.3, StreamAnalyser 1.2 and ESPCB7.0 Alfa were saved to three files named ESP_Case3.xls, StreamAnalyser_Case3.xls, and ESPCB_Case3.xls, respectively (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. For ESPCB, the deviations of the test results from the experimental data are within ±10 percent and, therefore, are acceptable. However, for ESP and StreamAnalyzer, the deviations of the test data at a high $CaCl_2$ concentration (>1.2 molal) are 15.4 percent, which is higher than the ±10 percent target. Therefore, ESP and StreamAnalyzer should be used with caution for solutions containing multi-component salts.

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 to determine the ability of the OLI packages 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 ESP6.6/CSP2.3, StreamAnalyser1.2, and ESPCB7.0 Alfa were saved to three files named ESP_Case4.xls, StreamAnalyser_Case4.xls, and ESPCB_Case4.xls, respectively (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

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

Temp (°C)	Fixed Salt Concentrations (m)			Solubility of $MgCl_2$ (m)						
					ESP		ESPCB		StreamAnalyzer	
	$CaCl_2$	KCl	NaCl	Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
50	0.000	0.021	0.050	6.457	6.192	-4.107	6.182	-4.268	6.192	-4.110
	0.086	0.022	0.049	6.366	6.146	-3.467	6.121	-3.847	6.144	-3.487
	0.182	0.022	0.050	6.279	6.094	-2.947	6.049	-3.662	6.093	-2.949
	0.376	0.023	0.051	5.981	5.989	0.133	5.905	-1.269	5.989	0.129
	0.620	0.024	0.052	5.680	5.866	3.261	5.729	0.849	5.865	3.257
	0.768	0.025	0.051	5.391	5.792	7.437	5.619	4.221	5.793	7.442
	1.226	0.028	0.058	4.833	5.577	15.401	5.285	9.365	5.577	15.395
0	0.000	0.005	0.039	5.954	5.547	-6.822	5.541	-6.928	5.547	-6.824
	0.127	0.005	0.040	5.754	5.459	-5.134	5.440	-5.457	5.459	-5.136
	0.274	0.005	0.040	5.519	5.357	-2.928	5.321	-3.587	5.357	-2.932
	0.538	0.005	0.042	5.175	5.176	0.021	5.117	-1.119	5.176	0.018
	0.880	0.006	0.041	4.697	4.946	5.314	4.835	2.949	4.946	5.310
	1.042	0.006	0.044	4.546	4.839	6.444	4.732	4.101	4.838	6.439
	1.146	0.007	0.048	4.401	4.769	8.363	4.653	5.711	4.769	8.359

*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.

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 a function of concentration were calculated and compared with experimental data. The test was to determine the ability of the OLI packages to accurately calculate the vapor pressures of alkaline-earth-metal chloride solutions.

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

KCl Concentration (m)	Vapor Pressure (Bar)						
		ESP		ESPCB		StreamAnalyzer	
	Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
0.549	85.70	81.35	-5.07	81.24	-5.20	81.35	-5.07
0.966	84.78	80.27	-5.32	80.10	-5.53	79.22	-6.56
1.392	83.32	79.19	-4.95	79.01	-5.17	79.19	-4.95
1.904	81.78	77.95	-4.68	77.82	-4.85	77.95	-4.68
2.954	79.02	75.60	-4.32	75.64	-4.28	75.60	-4.32
3.388	77.62	74.71	-3.75	74.82	-3.61	74.71	-3.75
4.283	75.26	72.99	-3.01	73.21	-2.73	73.00	-3.00
4.528	74.56	72.56	-2.68	72.78	-2.39	72.56	-2.68

*Data are from Pabalan, 2002; original data are from Zarembo, et al., 1976.

References:

Pabalan, R.T. "Software Validation Report for Solcalc, Version 1.0." San Antonio, Texas: CNWRA. 2002.

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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 ESP6.6/CSP2.3, StreamAnalyser1.2, and ESPCB7.0 Alfa were saved to three files named ESP_Case5.xls, StreamAnalyser_Case5.xls and EXPCB_Case5.xls, respectively (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 (Weast, 1984) as shown in Table 5. The deviations of the test results from the experimental data are within ±10 percent and, therefore, considered acceptable.

Table 5. Comparison of Experimental and Calculated Vapor Pressure of $CaCl_2$ Solutions at 100 °C [212 °F]							
	Vapor Pressure (atm)						
		ESP		ESPCB		StreamAnalyzer	
$CaCl_2$ Concentration (m)	Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
0.5	0.978	0.974	-0.339	0.975	-0.278	0.974	-0.340
1	0.948	0.946	-0.147	0.948	0.005	0.946	-0.147
2	0.875	0.871	-0.380	0.876	0.162	0.871	-0.380
3	0.781	0.776	-0.567	0.784	0.454	0.776	-0.567
4	0.682	0.671	-1.578	0.682	-0.052	0.671	-1.578
5	0.580	0.568	-1.918	0.579	-0.021	0.568	-1.919
*CRC Handbook of Chemistry and Physics. Lide, D.R. ed. 77th Edition. p. 5–109. 1997.							

5.6 Test Case 6—Lowering of Vapor Pressure by $NaNO_3$, NaOH, $NaHSO_4$, and $NaHCO_3$ in Aqueous Solutions at 100 °C [212 °F]

The vapor pressures of $NaNO_3$, NaOH, $NaHSO_4$, and $NaHCO_3$ solutions were calculated according to the validation plan. However, $NaHCO_3$ involves a large amount of CO_2 and it is not clear if the partial pressure of CO_2 was included in the measured pressure for the determination of the lowering of the vapor pressure in the original experiment. Therefore, the results from the $NaHCO_3$ solution were not used in this report. Only the calculated data for $NaNO_3$, NaOH, and $NaHSO_4$ solutions were compared with the experimental data.

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 ESP6.6/CSP2.3, StreamAnalyser1.2, and ESPCB7.0 Alfa were saved to three files named ESP_Case6.xls, StreamAnalyser_Case6.xls, and ESPCB_Case6.xls, respectively (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 (Weast, 1984), as shown in Table 6. The deviations of the test results from the experimental data are within ±10 percent and, therefore, considered acceptable, except in the case with $NaHSO_4$ at high concentrations for the ESP and StreamAnalyzer. The ESP and StreamAnalyzer for high concentrations of salt solutions (>10 molal) should be used with caution.

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 NaNO3 Solution (atm)						
		ESP		ESPCB		StreamAnalyzer	
NaNO3 Concentration (m)	Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
2	0.939	0.938	-0.173	0.937	-0.259	0.938	-0.174
4	0.881	0.882	0.142	0.889	0.835	0.882	0.141
6	0.827	0.829	0.282	0.848	2.598	0.829	0.282
8	0.779	0.778	-0.181	0.811	4.130	0.778	-0.181
10	0.738	0.730	-1.193	0.776	5.057	0.730	-1.193
	Vapor Pressure of NaOH Solution (atm)						
		ESP		ESPCB		StreamAnalyzer	
NaOH Concentration (m)	Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
2	0.937	0.930	-0.656	0.932	-0.528	0.930	-0.657
4	0.859	0.854	-0.533	0.856	-0.331	0.854	-0.534
6	0.773	0.771	-0.245	0.765	-1.068	0.771	-0.245
8	0.680	0.686	0.930	0.664	-2.337	0.686	0.928
10	0.587	0.603	2.694	0.562	-4.248	0.603	2.692
	Vapor Pressure of $NaHSO_4$ Solution (atm)						
		ESP		ESPCB		StreamAnalyzer	
$NaHSO_4$ Concentration (m)	Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
2	0.938	0.929	-0.926	0.928	-1.093	0.929	-0.926
4	0.868	0.848	-2.324	0.857	-1.305	0.848	-2.324
6	0.805	0.762	-5.354	0.789	-1.906	0.762	-5.355
8	0.750	0.688	-8.256	0.731	-2.531	0.688	-8.256
10	0.696	0.623	-10.402	0.676	-2.837	0.623	-10.402
*CRC Handbook of Chemistry and Physics. Lide, D.R. ed. 77th Edition. p. 5–109. 1997.							

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 to determine the ability of the OLI Packages 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 ESP6.6/CSP2.3, StreamAnalyser1.2, and ESPCB7.0Alfa were saved to three files named ESP_Case7.xls, StreamAnalyser_Case7.xls, and ESPCB_Case7.xls, respectively (see Appendix). These files list the temperature and pressure used in the calculation, the resulting ionic strength, and the calculated concentrations of Na^+ and NO_3^-, Cl^-, and K^+. The calculated deliquescence points are the ratio between the vapor pressure of the three saturated salts and the vapor pressure of water or the activity of water directly reported in the StreamAnalyzer. The calculated values were compared with the deliquescence point measured in the experiments (Yang, et al., 2001), as shown in Table 7. The deviations of the test result obtained with the ESPCB from the experimental data are within ±10 percent and, therefore, considered acceptable. However, the deviations of the test results from both the ESP and the StreamAnalyzer are approximately 23 percent. This large discrepancy probably occurred because the ionic strength of the solution (26.2 calculated by ESPCB) was close to the upper limit of the ESP and StreamAnalyzer. Therefore, only ESPCB can be used to calculate the deliquescence properties of the salts. For those systems ESPCB does not support, ESP or StreamAnalyzer can only be used for qualitative analysis, such as examining the trend of the deliquescence as the compositions change.

Table 7. Comparison of Experimental and Calculated Deliquescence Relative Humidity of NaNO3-NaCl-KNO3 Mixture at 86 °C [186.8 °F]

Deliquescence Relative Humidity of NaNO3-NaCl-KNO3 Saturated Solution (%)						
	ESP		ESPCB		StreamAnalyzer	
Measured*	Calc.	%Dev	Calc.	%Dev	Calc.	%Dev
43.4	53.2	22.7	46.8	7.8	53.4	23.0

*Yang, L., R.T. Pabalan, and L. Browning. "Experimental Determination of the Deliquescence Relative Humidity and Conductivity of Multicomponent Salt Mixtures." Scientific Basis for Nuclear Waste Management XXV. Symposium Proceedings 713. Warrendale, Pennsylvania: Materials Research Society. pp. 135--142. 2002.

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5.8 Test Case 8—Stability Diagram for Nickel-Water System

The stability diagram of nickel-water system at 25 °C [77 °F] was calculated and compared with a published stability diagram. The test was to determine the ability of the OLI ESP6.5/CSP2.3 to accurately calculate the stability diagram of metals in solution.

5.8.1 Test Input

The input temperature used was 25 °C [77 °F]. HCl and NaOH were used as the acid and base titrants, respectively, for pH adjustment. Only water was specified in the input stream. The concentration of Ni^{2+} was set at the trace species amount (1×10^{-6} M), which is specified in the Option menu under Trace Species Amount submenu.

5.8.2 Test Procedure

The test was run in the pH range of 0 to 14 and the potential range of -1.0 to 2.0 V. An E–pH diagram under standard state (1 M activity for dissolved species) was produced.

5.8.3 Test Results

A hard copy of the output stability diagram (E–pH diagram) from the run with ESP6.6/CSP2.3 is shown in Figure 1. A published E-pH diagram for the same system is shown in Figure 2 (Pourbaix, 1974). The important lines (2, 3, 6, 7, 9, 11, and 14) in the two diagrams are close to each other. Detailed comparisons between the calculated and the published potential and pH values for selected points are presented in Table 8. The deviations of the calculated potential results from the published data are within ±0.15 V from values showing on the published E–pH diagrams, and thus considered acceptable. The deviations of the calculated pH results from the published data are less than ±0.1 for data points D, E, and F. However, the deviation of the calculated pH results from the published data for points B and C are approximately 0.6. These data points (B and C) involve $Ni(OH)_2$ for which the reported thermodynamic data vary significantly (Bard, et al., 1985). The large variation in these data corresponds to a pH variation in the range of 5.4 to 7.1. Therefore, the deviations for pH values are also considered acceptable even though the acceptable pH error was originally set to ±0.3 in the validation plan (Yang, 2002).

Table 8. Comparison of the Calculated pH and Potential Values with the Data from Published Literatures

	pH			Potential		
Data Point	Calculated	Reference*	Error	Calculated	Reference*	Error
B	5.44	6.03	-0.59	0.63	0.52	0.10
C	5.46	6.04	-0.58	-0.21	-0.24	0.03
D	13.99	14.01	-0.02	0.71	0.59	0.12
E	14.00	13.99	0.01	0.17	0.06	0.11
F	14.00	13.99	0.02	-0.74	-0.72	-0.03

*Pourbaix, M. "Reference: Atlas of Electrochemical Equilibriua." 2nd Edition. p. 333. Houston, Texas: NACE International. 1974.

5.9 Test Case 9—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 to determine the ability of the ESPCB software to accurately calculate the solution properties of extremely concentrated aqueous solutions.

5.9.1 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.

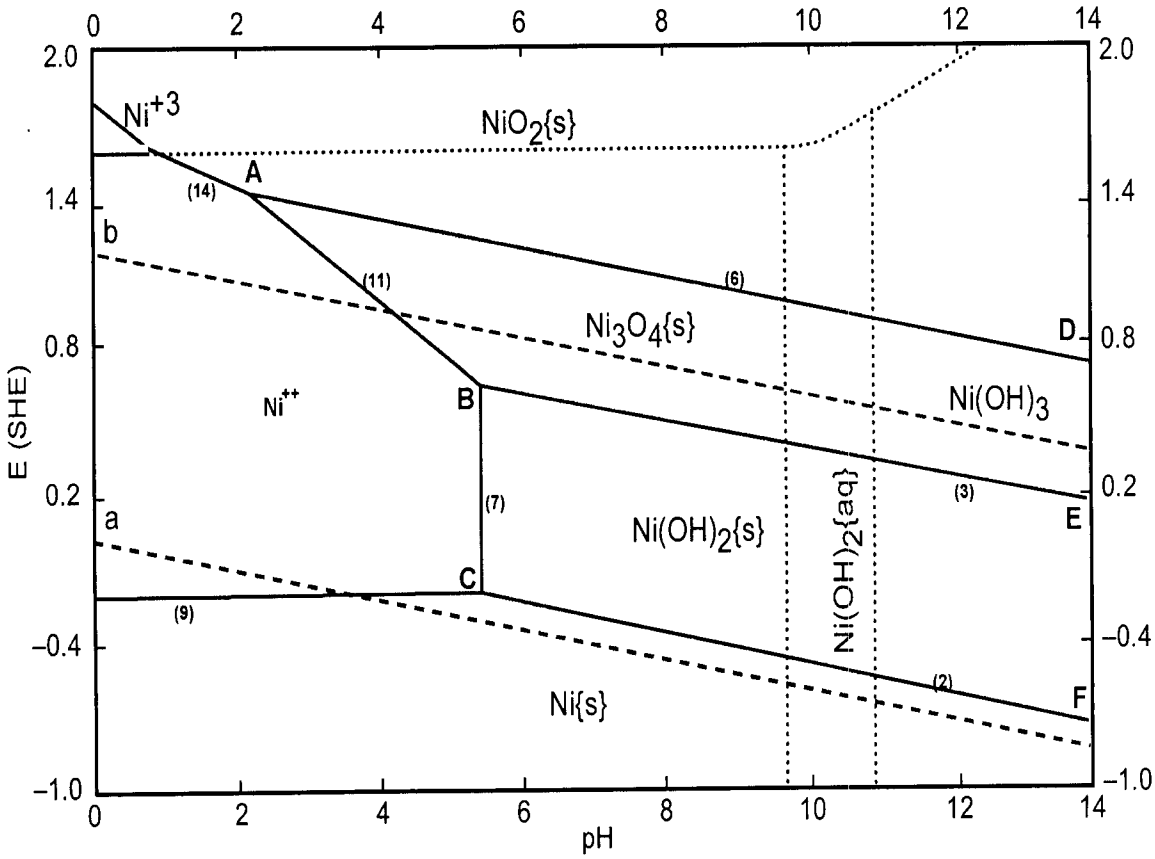

Figure 1. Calculated E-pH Diagram for Nickel-Water System

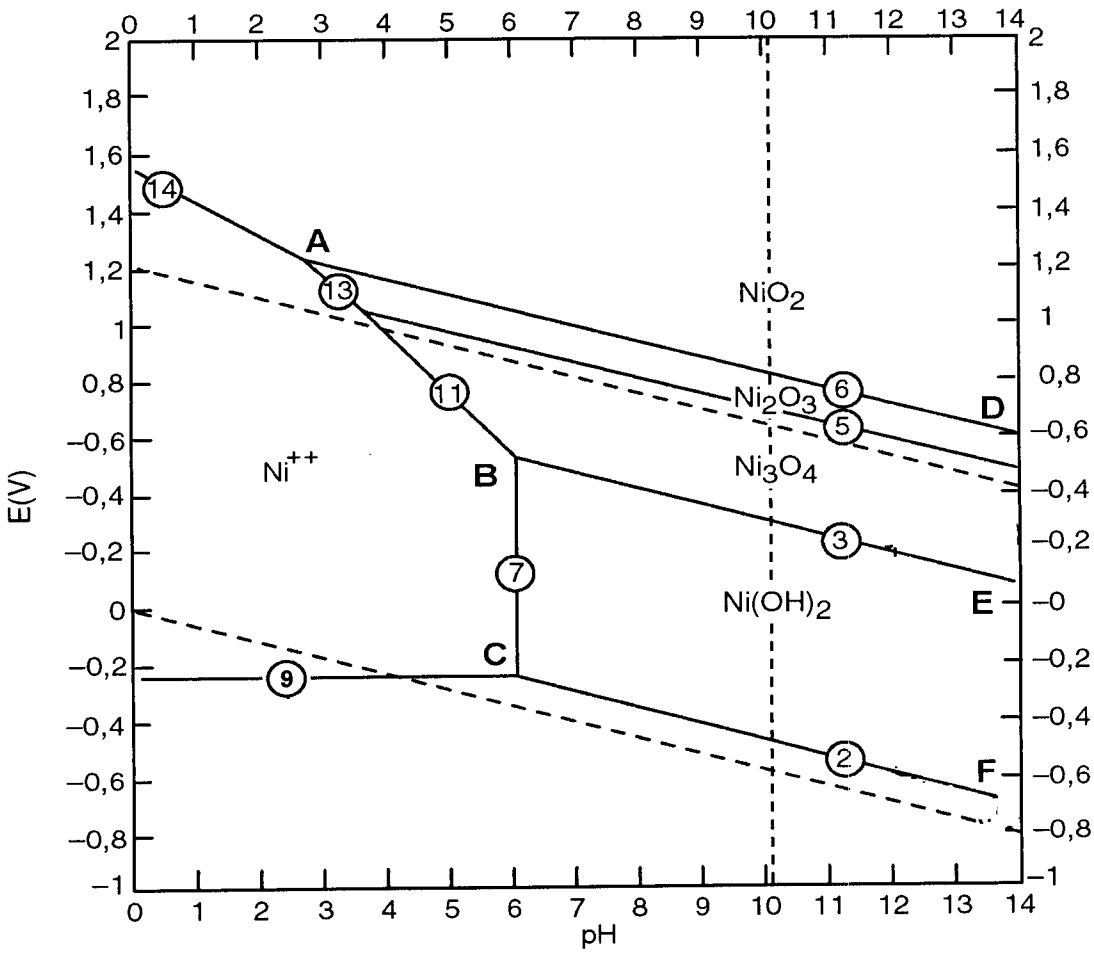

Figure 2. E-pH Diagram for the Nickel Water System from Published Literature (Pourbaix, 1974)

5.9.2 Test Procedure

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

5.9.3 Test Results

The results of calculations with ESPCB7.0 Alfa were saved to EXPCB_ Case9.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 9. The deviations of the test results from the experimental data are within ±10 percent and, therefore, considered acceptable.

Table 9. Comparison of the Calculated Solubilities with the Experimental Values for Concentrated $NaNO_3$ and NaOH Solutions

Salt	Temp (°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
	S (m)	19.8	22.2	24.0	29.1	33.9	45.2	48.3	60.0
	%Dev	1.18	1.60	1.74	0.90	0.95	1.39	1.05	0.22
NaOH	Temp (°C)	30	40	50	60	80	110	192	—
	Expt*	29.8	32.3	36.3	43.5	78.3	91.3	130.3	—
	S (m)	29.6	32.6	36.8	41.3	78.4	87.3	131.6	—
	%Dev	-0.64	1.21	1.41	-4.99	0.20	-4.32	1.06	—

*Linke, W.F. and A. Seidell. "Solubilities of Inorganic and Metal-Organic Compounds K-Z." Vol. II, 4th Edition. Washington, DC: American Chemical Society. pp. 1,070 and 1,084. 1965.

5.10 Test Case 10—Lowering of Vapor Pressure by $NaNO_3$, NaOH, $NaHSO_4$, and $NaHCO_3$ in Aqueous Solutions at 100 °C [212 °F] Using Private Databases

This test case was specified in the validation test plan (Yang, 2002).

According to the user manual, in addition to the public database, OLI simulation packages contain several private databases such as Geochem, Ceramic, and Corrosion. In most simulations, the public database contains all the thermodynamic data that are required. However, there are cases where some species required in a simulation cannot be found in the public database. In this case, one or more private databases that contain the required species must be activated by the user. The OLI engine will search the private databases first (according to the sequence in the activated private list) for all the species involved in the simulation. If there are still species that are not found in the specified private databases, the public database will be activated. During the test, it was learned that data for a required species are only stored in one of these databases. If they are in the public database, they cannot be found in any of the other databases. This originally planned test case could not be completed and was cancelled.

6 CONCLUSIONS

OLI ESP6.6/CSP2.3, StreamAnalyzer 1.2, and ESPCB 7.0 were 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/or KCl) in the temperature range from 40 to 150 °C [104 to 302 °F].
3. Solubility of $MgCl_2$ in $CaCl_2$-NaCl-KCl Solutions at 0 and 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 solutions at 100 °C [212 °F] at concentrations up to 5 M.
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. Stability diagram for a metal (Nickel) in a water system (EPS 6.6/CSP2.3 only).
9. Solubility of a salt ($NaNO_3$) and a hydroxide (NaOH) at concentrations beyond 30 M (ESPCB only).

Except for case 2, the results obtained with ESPCB 7.0 are acceptable. The vendor acknowledged that there was a problem with their data bank for some mixed salts (case 2) for ESPCB 7.0 and claimed that the problem with the NaCl-KCl system has been resolved for their future release of the software.

The results obtained with ESP6.6/CSP2.3 and StreamAnalyzer 1.2 are acceptable for cases 1, 2, 4, 5, 8 and 9; but not acceptable for cases 3, 6, and 7. In cases 3, 6 and 7, the results are from 10 to 23 percent off the experimentally obtained data. Therefore, ESP6.6/CSP2.3 and StreamAnalyzer1.2 should be used with caution for solutions containing multi-component salts or at ionic strength greater than 10 molal. When the ionic strength approaches the upper ionic strength limit of the software, 30 molal, ESP and StreamAnalyzer can only be used to perform qualitative analyses such as trend analysis.

7 REFERENCES

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Appendix

Case Data Files

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

Results from ESP:

ESP_Case1.xls
ESP_Case2.xls
ESP_Case3.xls
ESP_Case4.xls
ESP_Case5.xls
ESP_Case6.xls
ESP_Case7.xls
ESP_Case8.xls

Test Results from ESPCB
ESPCB_Case1.xls
ESPCB_Case2.xls
ESPCB_Case3.xls
ESPCB_Case4.xls
ESPCB_Case5.xls
ESPCB_Case6.xls
ESPCB_Case7.xls
ESPCB_Case9.xls

Test Results from SteamAnalyzer

StreamAnalyser_Case1.xls
StreamAnalyser_Case2.xls
StreamAnalyser_Case3.xls,
StreamAnalyser_Case4.xls,
StreamAnalyser_Case5.xls,
StreamAnalyser_Case6.xls,
StreamAnalyser_Case7.xls,