SOFTWARE VALIDATION REPORT FOR LABANALYZER VERSION 2.0, ENVIRONMENTAL SIMULATION PROGRAM VERSION 7.0, AND CORROSION ANALYZER VERSION 2.0

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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 LabAnalyzer Version 2.0, Environmental Simulation Program (ESP) Version 7.0, and Corrosion Analyzer Version 2.0. These software packages were developed by OLI Systems, Inc. (Morris Plains, New Jersey). Calculation results are documented in Electronic Scientific Notebook 716.

1 SCOPE OF THE VALIDATION

This report documents the validation of the simulation software packages LabAnalyzer Version 2.0, Environmental Simulation Program (ESP) Version 7.0, and Corrosion Analyzer Version 2.0 based on the software validation test plan (Yang, 2002) and the test cases used in validating StreamAnalyzer Version 1.2, CSP Version 2.3, and ESP Version 6.6 (Yang, 2003). The validation involved comparing calculated results with experimental data available in the literature.

LabAnalyzer Version 2.0, ESP Version 7.0, and Corrosion Analyzer Version 2.0 are software packages of the simulation family developed by OLI Systems, Inc. (Morris Plains, New Jersey). The family of simulation packages includes ESP, Corrosion Analyzer, StreamAnalyzer, and LabAnalyzer. ESP is used for evaluating the thermodynamic properties of different streams in a chemical process in industrial and environmental applications. Corrosion Analyzer 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. LabAnalyzer is packaged as stand-alone software with a user-friendly graphic interface for evaluating the thermodynamic behavior of components of single or multiple aqueous streams. In contrast to previous versions, ESP Version 7.0 and Corrosion Analyzer Version 2.0 have a new chemistry model, referred to as the Mixed Solvent Electrolyte (MSE) model, and associated new thermodynamic parameters. The standard chemistry model of ESP and Corrosion Analyzer 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, and is 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 ESP Version 7.0 were tested, but only the standard chemistry model of Corrosion Analyzer Version 2.0 was tested. The chemistry model of LabAnalyzer is applicable to aqueous systems with ionic strengths up to 30 molal.

The scope of the validation was within the following ranges:

Temperature:	0 to 300 °C [32 to 572 °F]
Pressure:	0 to 1,480 atm [0 to 21,750 psi]
Ionic Strength:	0 to 30 molal for ESP and Corrosion Analyzer with the standard chemistry model and for LabAnalyzer; 0 to 130 molal for ESP with the MSE chemistry model

2 SYSTEM REQUIREMENTS

2.1 Software

LabAnalyzer Version 2.0, ESP Version 7.0, and Corrosion Analyzer Version 2.0 run in a Microsoft® Windows environment (98, ME, NT, 2000, and XP). The validation tests were conducted in Windows 2000.

2.2 Hardware

LabAnalyzer Version 2.0, ESP Version 7.0, and Corrosion Analyzer Version 2.0 run 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. LabAnalyzer, ESP, and Corrosion Analyzer also support graphical output to printers.

3 PREREQUISITES

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

4 ASSUMPTIONS AND CONSTRAINTS

LabAnalyzer Version 2.0 and the standard chemistry model of ESP Version 7.0 and Corrosion Analyzer Version 2.0 are 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, ESP Version 7.0 and Corrosion Analyzer Version 2.0 have 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 ESP Version 7.0 and Corrosion Analyzer 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. The limitations for ESP Version 7.0 and Corrosion Analyzer Version 2.0 using the MSE model are

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 LabAnalyzer Version 2.0 and ESP 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 [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 the bubble point at temperatures equal to or above 100 °C [212 °F].

5.1.3 Test Results

The results of calculations with LabAnalyzer Version 2.0 and ESP Version 7.0 (standard and MSE models) were saved to three files named LabAnalyzer2.0_Case1.xls, ESP7.0_Case1.xls, and ESP7.0-MSE_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 by Liu and Lindsay (1972) and Linke (1965), as shown in Table 1. The deviations (% Dev) of the test results from the experimental data are within ± 10 percent and, therefore, are acceptable. The ± 10 percent criterion is specified 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.

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
ESP Version 7.0	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	-1.91	-2.41
ESP (MSE) Version 7.0	S(m)	6.14	6.27	6.48	6.72	6.97	7.24	7.52	7.88	8.35	8.94	9.67	10.42
	%Dev‡	-0.18	-0.03	0.23	0.60	0.55	0.52	-0.70	-1.18	-1.05	-0.51	0.21	0.04
LabAnalyzer Version 2.0	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	-1.91	-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.

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 LabAnalyzer Version 2.0 and ESP Version 7.0 to accurately calculate the solubility of a mineral salt in a solution containing two types of dissolved salts 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. Conversely, 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 to or above 100 °C [212 °F].

5.2.3 Test Results

The results of calculations with LabAnalyzer Version 2.0 and ESP Version 7.0 (standard and MSE model) were saved to three files named LabAnalyzer2.0_Case2.xls, ESP7.0_Case2.xls, and ESP7.0-MSE_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 by Linke (1965), as shown in Table 2. The deviations of the test results obtained with LabAnalyzer Version 2.0 and ESP Version 7.0 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 LabAnalyzer Version 2.0 and ESP Version 7.0 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.

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

Solubility of NaCl in KCl Solutions

Temp. (°C)*	KCl Conc.† (m)	Solubility of NaCl (m)						
			Environmental Simulation Program (ESP) Version 7.0		ESP Version 7.0 Mixed Solvent Electrolyte (MSE)		LabAnalyzer Version 2.0	
		Measured‡	Calc§	%Dev‖	Calc§	%Dev‖	Calc§	%Dev‖
40	0	6.217	6.224	0.12	6.207	-0.16	6.225	0.12
	0.87	5.801	5.795	-0.11	5.767	-0.59	5.795	-0.11
	1.407	5.577	5.540	-0.67	5.504	-1.30	5.540	-0.67
	1.733	5.409	5.389	-0.38	5.348	-1.13	5.389	-0.38
	2.566	5.12	5.065	-1.07	4.961	-3.11	5.065	-1.07
100	0	6.68	6.690	0.15	6.720	0.60	6.690	0.15
	2.046	5.749	5.694	-0.96	5.749	-0.01	5.694	-0.96
	4.024	4.791	4.856	1.36	4.901	2.29	4.856	1.36
	4.086	4.94	4.832	-2.19	4.875	-1.31	4.832	-2.19
150	0	7.198	7.249	0.71	7.235	0.52	7.249	0.71
	4.024	5.698	5.439	-4.55	5.609	-1.56	5.439	-4.55
	5.365	5.185	4.953	-4.48	5.141	-0.85	4.953	-4.48

Solubility of KCl in NaCl Solutions

Temp. (°C)*	KCl Conc.† (m)	Solubility of KCl (m)						
			ESP Version 7.0		ESP Version 7.0 (MSE)		LabAnalyzer Version 2.0	
		Measured‡	Calc§	%Dev‖	Calc§	%Dev‖	Calc§	%Dev‖
40	0	5.37	5.416	0.85	5.428	1.08	5.416	0.85
	1.748	4.28	4.203	-1.79	4.288	0.18	4.203	-1.79
	1.827	4.21	4.153	-1.36	4.240	0.72	4.153	-1.36
	3.486	3.32	3.193	-3.83	3.320	-0.02	3.193	-3.83
	3.592	3.28	3.138	-4.33	3.266	-0.42	3.138	-4.33
100	0	7.54	7.491	-0.65	7.518	-0.29	7.491	-0.65
	1.717	6.44	6.256	-2.85	6.414	-0.40	6.256	-2.85
	1.744	6.32	6.238	-1.30	6.398	1.23	6.238	-1.30
	2.567	5.90	5.697	-3.44	5.911	0.19	5.697	-3.44

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								
		Solubility of KCl (m)						
	NaCl Conc.† (m)		**ESP Version 7.0**		**ESP Version 7.0 Mixed Solvent Electrolyte (MSE)**		**LabAnalyzer Version 2.0**	
		Measured‡	**Calc§**	**%Dev‖**	**Calc§**	**%Dev‖**	**Calc§**	**%Dev‖**
150	0	9.02	9.044	0.27	9.061	0.46	9.044	-0.27
	1.711	8.13	7.831	-3.67	8.096	-0.42	7.831	-3.67
	2.567	7.64	7.274	4.80	7.650	0.14	7.274	-4.80
	3.422	7.15	6.752	-5.57	7.230	1.11	6.752	-5.57
	4.278	6.71	6.266	-6.62	6.833	1.83	6.266	-6.62

Solubility of NaCl and KCl in a NaCl-KCl Mixture							
		KCl Solubility (m)			**NaCl Solubility (m)**		
Calculation	**Temp. (°C)***	**Measured‡**	**Calc§**	**%Dev‖**	**Measured‡**	**Calc§**	**%Dev‖**
ESP Version 7.0	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
ESP Version 7.0 (MSE)	40	2.627	2.653	0.98	5.008	4.922	-1.73
	100	4.734	4.843	2.29	4.708	4.577	-2.79
	150	6.518	6.632	1.74	4.791	4.732	-1.23
Lab Analyzer Version 2.0	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
†Conc.—concentration
‡ 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.
§Calc—calculation
‖% Dev—deviation

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 LabAnalyzer Version 2.0 and ESP Version 7.0 (standard and MSE models) were saved to three files named LabAnalyzer2.0_Case3.xls, ESP7.0_Case3.xls, and ESP7.0-MSE 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 difference between the experimental value and the values calculated using ESP 7.0 and LabAnalyzer Version 2.0 is 15.37 percent. Although this difference is 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 LabAnalyzer Version 2.0 and ESP Version 7.0 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 LabAnalyzer Version 2.0 and ESP Version 7.0 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 LabAnalyzer Version 2.0 and ESP Version 7.0 (standard and MSE model) were saved to three files named LabAnalyzer2.0_Case4.xls, ESP7.0_Case4.xls and ESP7.0-MSE_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 LabAnalyzer Version 2.0 and ESP Version 7.0 to accurately calculate the vapor pressures of alkaline-earth-metal chloride solutions.

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)*						
					Environmental Simulation Program (ESP) Version 7.0		ESP Version 7.0 Mixed Solvent Electrolyte (MSE)		LabAnalyzer Version 2.0	
	$CaCl_2$	KCl	NaCl	Meas‡	Calc§	%Dev‖	Calc§	%Dev‖	Calc§	%Dev‖
50	0.000	0.021	0.050	6.457	6.192	-4.107	6.195	-4.064	6.192	-4.108
	0.086	0.022	0.049	6.366	6.144	-3.484	6.144	-3.486	6.144	-3.485
	0.182	0.022	0.050	6.279	6.093	-2.949	6.090	-3.005	6.093	-2.949
	0.376	0.023	0.051	5.981	5.989	0.129	5.978	-0.059	5.989	0.128
	0.620	0.024	0.052	5.680	5.865	3.250	5.842	2.854	5.865	3.252
	0.768	0.025	0.051	5.391	5.793	7.442	5.762	6.869	5.792	7.434
	1.226	0.028	0.058	4.833	5.575	15.367	5.516	14.144	5.576	15.370
0	0.000	0.005	0.039	5.954	5.547	-6.823	5.536	-7.013	5.547	-6.823
	0.127	0.005	0.040	5.754	5.459	-5.135	5.437	-5.508	5.459	-5.135
	0.274	0.005	0.040	5.519	5.357	-2.930	5.323	-3.547	5.357	-2.930
	0.538	0.005	0.042	5.175	5.176	0.018	5.117	-1.126	5.176	0.018
	0.880	0.006	0.041	4.697	4.946	0.000	4.850	-1.948	4.946	0.000
	1.042	0.006	0.044	4.546	4.838	0.000	4.722	-2.394	4.838	0.000
	1.146	0.007	0.048	4.401	4.769	0.000	4.640	-2.696	4.769	0.000

*The solubility controlling phase is $MgCl_2 \cdot 6H_20$
†°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.
§Calc—calculation
‖%Dev—deviation

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.

Table 4. Comparison of Experimental and Calculated Vapor Pressure of KCl Solutions at 300 °C [572 °F]							
KCl Concentration (m)	Vapor Pressure (Bar)						
	Measured*	Environmental Simulation Program (ESP) Version 7.0		ESP Version 7.0 Mixed Solvent Electrolyte (MSE)		LabAnalyzer Version 2.0	
		Calc†	%Dev‡	Calc†	%Dev.‡	Calc†	%Dev‡
0.549	85.70	81.37	-5.06	80.03	-6.61	81.36	-5.06
0.966	84.78	80.28	-5.31	78.97	-6.86	80.28	-5.31
1.392	83.32	79.21	-4.93	77.93	-6.47	79.21	-4.93
1.904	81.78	77.97	-4.66	76.73	-6.18	77.97	-4.66
2.954	79.02	75.64	-4.28	74.36	-5.89	75.64	-4.28
3.388	77.62	74.75	-3.70	73.41	-5.43	74.75	-3.70
4.283	75.26	73.04	-2.95	71.45	-5.07	73.04	-2.95
4.528	74.56	72.61	-2.62	70.91	-4.90	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.
†Calc—calculation
‡%Dev—deviation

5.5.3 Test Results

The results of calculations with LabAnalyzer Version 2.0 and ESP Version 7.0 (standard and MSE models) were saved to three files named LabAnalyzer2.0_Case5.xls, ESP7.0_Case5.xls, and ESP7.0-MSE_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.

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

The vapor pressures of $NaNO_3$, NaOH, and $NaHSO_4$ solutions were calculated and compared with 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.

Table 5. Comparison of Experimental and Calculated Vapor Pressure of $CaCl_2$ Solutions at 100 °C [212 °F]							
$CaCl_2$ Concentration (m)	Vapor Pressure (atm)*						
		Environmental Simulation Program (ESP) Version 7.0		ESP Version 7.0 Mixed Solvent Electrolyte (MSE)		LabAnalyzer Version 2.0	
	Measured†	Calc‡	%Dev§	Calc‡	%Dev§	Calc‡	%Dev§
0.5	0.978	0.974	-0.33	0.963	-1.54	0.974	-0.33
1	0.948	0.946	-0.14	0.947	-0.02	0.946	-0.14
2	0.875	0.871	-0.37	0.873	-0.24	0.871	-0.37
3	0.781	0.776	-0.56	0.778	-0.30	0.776	-0.56
4	0.682	0.672	-1.57	0.676	-0.96	0.672	-1.57
5	0.580	0.569	-1.91	0.576	-0.63	0.569	-1.91

*atm—atmosphere
†Lide, D.R., ed. *CRC Handbook of Chemistry and Physics*. 77th Edition. Boston, Massachusetts: CRC Press. 1997.
‡Calc—calculation
§% Dev—deviation

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 LabAnalyzer 2.0 and ESP Version 7.0 (standard and MSE models) were saved to three files named LabAnalyzer2.0_Case6.xls, ESP7.0_Case6.xls, and ESP7.0-MSE_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 ESP Version 2.0 and LabAnalyzer 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 LabAnalyzer Version 2.0 and ESP Version 7.0 for Test Case 6 are considered acceptable, but caution is advised when applying the standard chemistry model of ESP Version 7.0 and LabAnalyzer Version 2.0 for aqueous solutions containing high concentrations of $NaHSO_4$.

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)*						
		Environmental Simulation Program (ESP) Version 7.0		ESP Version 7.0 Mixed Solvent Electrolyte (MSE)		LabAnalyzer Version 2.0	
$NaNO_3$ Concentration (m)	Measured†	Calc‡	%Dev§	Calc‡	%Dev§	Calc‡	%Dev§
2	0.939	0.938	-0.15	0.935	-0.50	0.938	-0.15
4	0.881	0.879	-0.21	0.877	-0.49	0.879	-0.21
6	0.827	0.825	-0.20	0.825	-0.25	0.825	-0.20
8	0.779	0.775	-0.49	0.777	-0.31	0.775	-0.49
10	0.738	0.730	-1.19	0.733	-0.78	0.730	-1.13
	Vapor Pressure of NaOH Solution (atm)						
		ESP Version 7.0		ESP Version 7.0 (MSE)		LabAnalyzer Version 2.0	
NaOH Concentration (m)	Measured†	Calc‡	%Dev§	Calc‡	%Dev§	Calc‡	%Dev§
2	0.937	0.931	-0.65	0.927	-1.07	0.931	-0.65
4	0.859	0.854	-0.53	0.844	-1.72	0.854	-0.53
6	0.773	0.771	-0.24	0.756	-2.27	0.771	-0.24
8	0.680	0.686	0.94	0.668	-1.80	0.686	0.94
10	0.587	0.603	2.70	0.585	-0.38	0.603	2.70
	Vapor Pressure of $NaHSO_4$ Solution (atm)						
		ESP Version 7.0		ESP Version 7.0 (MSE)		LabAnalyzer Version 2.0	
$NaHSO_4$ Concentration (m)	Measured†	Calc‡	%Dev§	Calc‡	%Dev§	Calc‡	%Dev§
2	0.938	0.929	-0.92	0.927	-1.17	0.929	-0.92
4	0.868	0.848	-2.32	0.858	-1.14	0.848	-2.32
6	0.805	0.762	-5.35	0.797	-0.98	0.762	-5.35
8	0.750	0.689	-8.25	0.742	-1.07	0.689	-8.25
10	0.696	0.623	-10.40	0.695	-0.15	0.623	-10.40

*atm—atmosphere
†Lide, D.R. *CRC Handbook of Chemistry and Physics*. D.R. Lide, ed. 77th Edition. Boston, Massachusetts: CRC Press. 1997.
‡Calc—calculation
§%Dev—deviation

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 LabAnalyzer Version 2.0 and ESP Version 7.0 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 LabAnalyzer 2.0 and ESP Version 7.0 (standard and MSE models) were saved to three files named LabAnalyzer2.0_Case7.xls, ESP7.0_Case7.xls, and ESP7.0-MSE_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 calculated deliquescence relative humidity 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 LabAnalyzer Version 2.0 and ESP Version 7.0 (MSE model only) from the experimental data are within ± 10 percent and, therefore, considered acceptable. On the other hand, the deliquescence relative humidity calculated using the standard chemistry model of ESP Version 7.0 deviates from the experimental value by 23 percent. The deviation is large because the calculated ionic strength of the solution (~ 41 molal) exceeds the maximum value (30 molal) that is valid for use with the standard chemistry model of ESP Version 7.0. For aqueous concentrations that exceed 30 molal, only the MSE chemistry model of ESP Version 7.0 should be used to calculate the deliquescence properties of the salts.

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 ESP Version 7.0 (MSE model only) 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 (%)						
	Environmental Simulation Program (ESP) Version 7.0		ESP Version 7.0 Mixed Solvent Electrolyte(MSE)		LabAnalyzer Version 2.0	
Measured*	Calculation	%Dev†	Calculation	%Dev†	Calculation	%Dev†
43.4	53.2	22.7	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 bubble point or precipitation point.

5.8.3 Test Results

The results of calculations with ESP Version 7.0 (MSE models) were saved to ESP7.0-MSE_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 and, therefore, considered acceptable.

5.9 Test Case 9—Stability Diagram for Nickel-Water System

The stability diagram of the 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 Corrosion Analyzer Version 2.0 to accurately calculate the stability diagram of metals in solution.

5.9.1 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 molal), which is specified in the Option menu under the Trace Species Amount submenu.

Table 8. Comparison of the Calculated Solubilities (molal) 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
	Calc.	19.2	21.4	23.0	28.6	33.6	46.4	50.2	60.0
	%Dev‡	-1.76	-2.10	-2.16	-1.02	-0.12	4.17	5.13	0.27
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	—
	Calc.	29.4	32.1	36.0	43.2	77.1	90.9	126.6	—
	%Dev‡	-1.35	-0.43	-0.61	-0.73	-1.42	-0.35	-2.78	—

* °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—deviation

5.9.2 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 was produced under standard state (1 molal activity for dissolved species).

5.9.3 Test Results

A copy of the output stability diagram (E-pH diagram) from the run with Corrosion Analyzer Version 2.0 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 9. 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 deviations of the calculated pH results from the published data for points B and C are approximately 0.6. These data points (B and C) for which the reported thermodynamic data vary significantly (Bard, et al., 1985) involve $Ni(OH)_2$. 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).

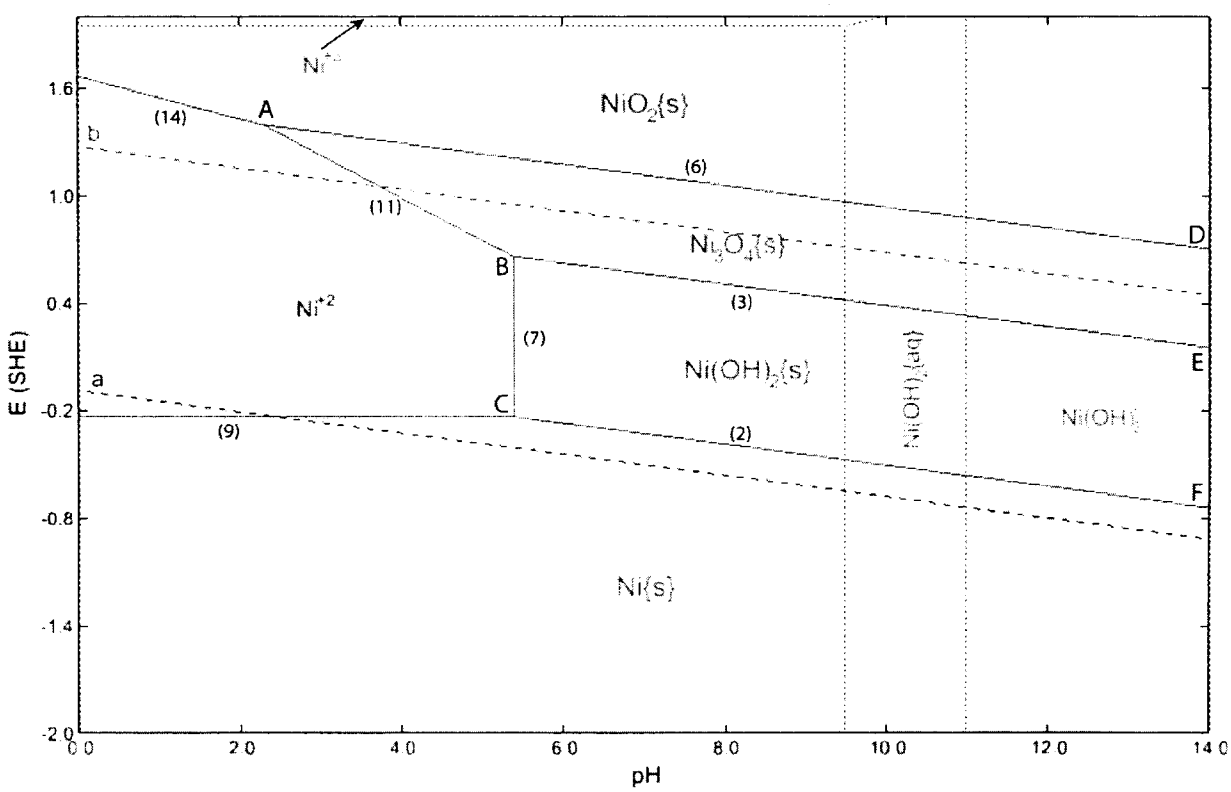

Figure 1. Calculated E-pH Diagram for Nickel-Water System

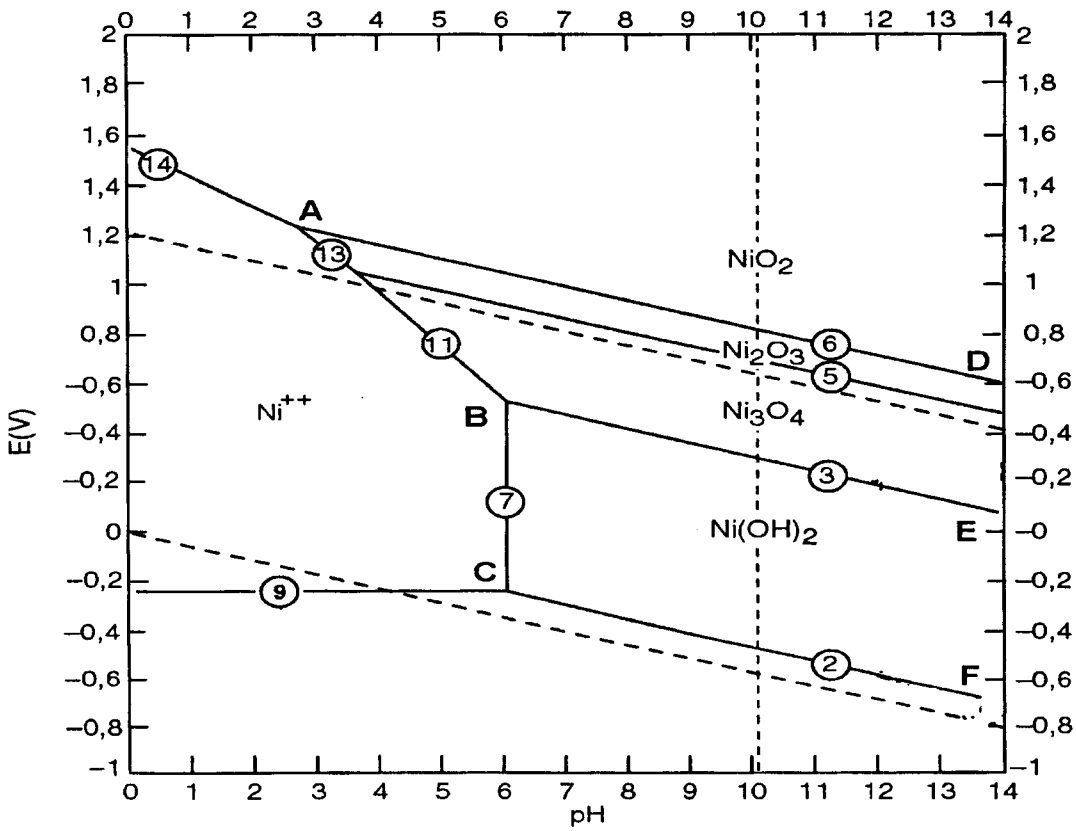

Figure 2. E-pH Diagram for the Nickel Water System From Published Literature (Pourbaix, 1974)

Table 9. Comparison of the Calculated pH and Potential Values With the Data From Published Literature

	pH			Potential(V_{SHE})†		
Data Point	**Calculated**	**Reference***	**Error**	**Calculated**	**Reference***	**Error**
B	5.39	6.03	-0.64	0.66	0.52	0.14
C	5.39	6.04	-0.65	-0.24	-0.24	0.00
D	14.00	14.01	-0.01	0.71	0.59	0.12
E	14.00	13.99	0.01	0.15	0.06	0.09
F	14.00	13.99	0.02	-0.74	-0.72	-0.02

*Pourbaix, M. "Atlas of Electrochemical Equilibria in Aqueous Solutions." 2nd Edition. Houston, Texas: NACE International. p. 333. 1974.
† SHE—standard hydrogen electrode

6 CONCLUSIONS

LabAnalyzer Version 2.0 and ESP Version 7.0 (standard and MSE chemistry models) 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 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 to 50 °C [32 to 122 °F]

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

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 (MSE model of ESP only)

Corrosion Analyzer Version 2.0 (standard chemistry model) was tested for the following case:

- Stability diagram for a metal (Nickel) in a water system

The results obtained with LabAnalyzer Version 2.0, ESP Version 7.0, and Corrosion Analyzer Version 2.0 are acceptable for all cases and can be used subject to the limits listed in Section 4.

7 REFERENCES

Bard, A., R. Parsons, and J. Jordan. *Standard Potentials in Aqueous Solution*. Chapter 12. New York City, New York: Marcel Dekker Publishers. 1985.

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. *Activity Coefficients in Electrolyte Solutions*. 2nd Edition. K.S. Pitzer, ed. 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.

Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. 2nd Edition. J. Franklin, English translation. p. 333. Houston, Texas: NACE International. 1974.

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 LabAnalyzer Version 1.2." San Antonio, Texas: CNWRA. 2003.

Yang, L. "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 LabAnalyzer Version 1.2." San Antonio, Texas: CNWRA. 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 ESP 7.0 using standard chemistry model

ESP7.0_Case1.xls
ESP7.0_Case2.xls
ESP7.0_Case3.xls
ESP7.0_Case4.xls
ESP7.0_Case5.xls
ESP7.0 _Case6.xls
ESP7.0_Case7.xls

Test results from ESP 7.0 using the MSE chemistry model

ESP7.0-MSE_Case1.xls
ESP7.0-MSE_Case2.xls
ESP7.0-MSE_Case3.xls
ESP7.0-MSE_Case4.xls
ESP7.0-MSE_Case5.xls
ESP7.0-MSE_Case6.xls
ESP7.0-MSE_Case7.xls
ESP7.0-MSE_Case8.xls

Test results from LabAnalyzer 2.0

LabAnalyzer2.0_Case1.xls
LabAnalyzer2.0_Case2.xls
LabAnalyzer2.0_Case3.xls
LabAnalyzer2.0_Case4.xls
LabAnalyzer2.0_Case5.xls
LabAnalyzer2.0_Case6.xls
LabAnalyzer2.0_Case7.xls

Test results from Corrosion Analyzer 2.0

CorrosionAnalyzer2.0_Case9