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ABSTRACT

The Fuel Conditioning Facility at the Idaho National Laboratory processes spent nuclear fuel from the Experimental Breeder Reactor II using electro-metallurgical treatment. To process fuel without waiting for periodic sample analyses to assess process conditions, an electrorefiner process model predicts the composition of the electrorefiner inventory and effluent streams. For the chemical equilibrium portion of the model, the two common methods for solving chemical equilibrium problems, *stoichiometric* and *non-stoichiometric*, were investigated. In conclusion, the *stoichiometric* method produced equilibrium compositions close to the measured results whereas the *non-stoichiometric* method did not.

Key Words: Pyrochemical processing; Electrorefiner; Chemical equilibrium; stoichiometric.

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INTRODUCTION

Electro-metallurgical treatment of spent nuclear fuel is performed in the Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL) as part of the Advanced Fuel Cycle Initiative (AFCI). The process treats spent fuel from the Experimental Breeder Reactor II (EBR-II) by separating uranium from the fission products and structural materials (cesium, sodium, steel cladding, etc.) in a vessel called an electrorefiner (ER) [1, 2]. Having process knowledge of the ER inventory prior to sample analysis is essential for timely operations and material accountability. A way to obtain this knowledge is to predict the mass and composition in the ER inventory and effluent streams without waiting for sampling and analysis, which are time consuming for FCF and the Analytical Laboratory. To serve this purpose, an ER process model was developed to predict the mass and composition of the ER inventory and its effluent streams using multi-component, multi-phase chemical equilibrium and electro-chemical transport from the anode(s) to the cathode(s). For the chemical equilibrium portion of the model, the author investigated two common approaches, defined as *stoichiometric* and *non-stoichiometric* [3], for determining chemical equilibrium compositions. The *non-stoichiometric* method minimizes the total Gibbs free energy by adjusting the quantity of the species directly while satisfying mass-balance constraints. The *stoichiometric* method adjusts the progress or extent of each chemical reaction to minimize the total Gibbs free energy in the system.

This paper briefly describes the Mark-IV electrorefiner, the loading of chemicals into the ER to establish initial conditions for processing spent fuel, the comparison of the results from the two chemical equilibrium methods to ER sample analyses, and conclusions. This is not a major investigation of the vast field of chemical equilibrium, but an answer to the question, "Given the choice between the stoichiometric or non-stoichiometric method, which produces an equilibrium composition in close agreement with the measured results obtained after the initial loading of chemicals into the Mark-IV electrorefiner?"

EXPERIMENTAL

Apparatus

The Mark-IV electrorefiner, a steel vessel one-meter tall with a one meter inside diameter maintained at 500 C, contains a salt bath and a cadmium bath (see Figure 1). Initially the system contained 4601 moles (195 kg) of lithium chloride (LiCl), 3159 moles (236 kg) of potassium chloride (KCl), and 4720 moles (531 kg) of cadmium (Cd) in the cadmium bath.

For the experiment, 84.08 moles (20 kg) of uranium metal was loaded into porous steel baskets and immersed into the salt bath followed by 126 moles (23 kg) of cadmium chloride ($CdCl_2$) to chemically oxidize the uranium in the baskets to uranium chloride via the chemical reaction shown in equation 1.

$$3CdCl_2 + 2U \leftrightarrow 3Cd + 2UCl_3 \qquad 1$$

At 773 K, the Gibbs free energies of formation for the $CdCl_2$ and UCl_3 species are -64.62 and -165.6 kcal / mole, respectively [4]. The elements uranium (U) and cadmium (Cd) have no free energy of formation. The Gibbs free energy of the chemical reaction in equation 1 is -3(-64.62) + -2(0) + 3(0) + 2(-165.6) = -137.3 kcal / mole of reaction, which makes it highly favorable for the uranium in the basket to react with the $CdCl_2$ and form UCl_3 in the salt bath.

Three days after placing the uranium and $CdCl_2$ in the salt bath, samples were taken from the salt bath and cadmium pool and analyzed at the Material and Fuels Complex in the Analytical Laboratory. Analysis of the cadmium showed no detectable uranium, lithium below its detection limit of 0.0028 wt% and potassium below its detection limit of 0.007 wt%. The basket contents were not analyzed after the experiment. Table 1 contains the analysis of nine samples taken from the salt bath.

Figure 2 shows the initial conditions in the Mark-IV ER. The two chemical reaction interfaces are the basket-salt interface and the salt-pool interface.The initial species are U_{metal} in the basket, LiCl, KCl, and $CdCl_2$ in the salt bath, and liquid cadmium in the pool. The possible final species are elemental Li, K, Cd, and U in the basket, LiCl, KCl, $CdCl_2$, and UCl_3 in the salt bath, and Li, K, Cd, and U in the cadmium pool. Knowing the measured composition of the salt and cadmium, the purpose of this experiment was to determine which free energy minimization method, *stoichiometric* or *non-stoichiometric*, was in close agreement with the measurements.

Free Energy Minimization

In a closed system at a given temperature and pressure, the total Gibbs free energy will decrease until it reaches a minimum [5]. Equation 2 shows the general criterion for chemical equilibrium in a multi-component, multi-phase system.

$$\mathrm{G}^t = \sum_a^A \sum_e^E n_{ea}\mu_{ea} \qquad 2$$

In equation 2, G^t represents the total Gibbs free energy of all the chemical species, with the terms n_{ea} and μ_{ea} representing, respectively, the moles and chemical potential of species e in phase a [6]. Equation 3 shows the chemical potential for a single species and a species in solution.

$$\mu_e = \begin{cases} \mu^*_{ea} & \text{single species, one phase} \\ \mu^*_{ea} + \mathrm{RT}\ln\left(\dfrac{\gamma_{ea} n_{ea}}{n_a}\right) & \text{multi-species in phase } a \end{cases} \qquad 3$$

In equation 3, μ^*_{ea} and γ_{ea} are, respectively, the standard state free energy and activity coefficient of species e in phase a. R is the ideal gas constant (1.987 cal / mole K) and T is the absolute temperature (773.15 K). The term n_a in equation 3 is the total moles (Σn_{ea}) in phase a.

Non-stoichiometric Method

The non-stoichiometric method determines the n_{ea} values that minimize the total Gibbs free energy in the system subject to the mass balance constraints [7], as shown in equation 4.

$$\begin{aligned} &\min G^t = \sum_a^A \sum_e^E n_{ea}\mu_{ea} && \text{subject to:} \\ &\sum_a^A \sum_e^E z_{mea} n_{ea} = T_m; && m = 1,2,\ldots,M \\ &n_{ea} \ge 0; && e = 1,2,\ldots,E \quad a = 1,2,\ldots,A \end{aligned} \qquad 4$$

In equation 4, M is the number of chemical elements in the system. E*A is the number of unique species in the system. For each n_{ea}, the z_{mea} terms in the **Z** matrix (called the formula matrix) represent the number of atoms of chemical element m per atom of n_{ea}. For example, $CdCl_2$ has z_{mea} values of 1 for the element cadmium and 2 for the element chlorine. T_m is the initial amount of moles of the element m and is assumed not to change from initial to final equilibrium conditions. For the initial loading of the Mark-IV ER, Table 2 contains the information to minimize the Gibbs free energy with the non-stoichiometric method.

Stoichiometric Method

The stoichiometric method [8] minimizes the total Gibbs free energy by adjusting the extent of reaction ($d\varepsilon_r$) incrementally (e.g., Newton-Raphson) for each chemical reaction r and using the ν_{er} terms in the stoichiometric matrix **V** to determine the n_e values that minimize G^t, as shown in equation 5.

$$\text{Determine } \delta\varepsilon_r \text{ from } \left(\frac{\partial^2 \mathrm{G}^t}{\partial \varepsilon_r^2}\right)_{\mathrm{T,P}} \cdot \delta\varepsilon_r = -\left(\frac{\partial \mathrm{G}^t}{\partial \varepsilon_r}\right)_{\mathrm{T,P}} \quad \text{to obtain}$$

$$\left(\frac{\partial \mathrm{G}^t}{\partial \varepsilon_r}\right)_{\mathrm{T,P}} = \sum_a^A \sum_e^E \left(\nu_{ear} \cdot \mu_{ea}\right) = 0 \qquad r = 1,2,\ldots,R \text{ reactions} \qquad 5$$

$$\text{where } n_{ea} = n_{ea} + \sum_r \left(\nu_{ear} \cdot \delta\varepsilon_r\right)$$

For a chemical reaction in the form of $\nu_a A + \nu_b B \leftrightarrow \nu_c C + \nu_d D$, the upper-case letters are the chemical species involved in the chemical reaction and the ν terms are the *stoichiometric coefficients* that balance the chemical reaction. For multiple reactions occurring in a system, the stoichiometric coefficients form the stoichiometric matrix V with a sign convention where ν_{er} is negative for *reactants* and positive for *products*. As shown in Figure 2, the chemical reaction interfaces are the salt-basket interface and the salt-pool interface. Figure 3 shows the independent sets of chemical reactions at these two interfaces and Table 2 contains the initial moles and necessary thermodynamic data.

Armed with the fundamental knowledge of the two methods and using the initial moles as the starting conditions (initial guess) for the iterations, predictions from both were compared to the sample analysis.

RESULTS

For the non-stoichiometric method, the Solver® function [9] in Microsoft Excel® converged and satisfied the constraints. The total Gibbs free energy went from an initial value of –435619 kcal to –435670 kcal. The stoichiometric method used the Newton-Raphson iteration method to minimize the Gibbs free energy by adjusting the extents of reaction. The total Gibbs free energy went from –435619 kcal (initial value) to –439005 kcal. Table 3 compares the salt and cadmium sample analysis to their initial compositions and the compositions predicted via the two chemical equilibrium methods. Figure 4 is a graph of the initial and final salt compositions.

Both Table 3 and Figure 4 show that the stoichiometric method predicted a salt composition in agreement with the measured results where the non-stoichiometric method did not.

A possible explanation for this disparity is the geometry of the Mark-IV electrorefiner. Normally, the formula matrix **Z**, used in the non-stoichiometric method, is closely related to the stoichiometric matrix **V**, used in the stoichiometric method, by the relationship $\mathbf{ZV} = \mathbf{0}$ [10] with the number of chemical reactions (R) equal to the number of possible species ($E*A$) minus the number of elements (M), or $R = EA - M$. Using the formula matrix **Z** in Table 2, the stoichiometric matrix satisfying the equation $\mathbf{ZV} = 0$ is shown in Table 4 and the corresponding chemical reactions shown in Figure 5.

But the two metal phases (basket and cadmium pool) in the Mark-IV ER are only in contact with the salt and not in contact with each other. Figure 5 shows chemical reactions between the basket and the cadmium pool, which is a phase boundary that does not exist in the Mark-IV ER. Therefore, the formula matrix Z **in Table 2 (used in the non-stoichiometric method) and the relationship** $ZV = 0$ **does not create a stoichiometric matrix** V **that represents the chemical reactions occurring in the Mark-IV ER, as seen when comparing** Figure 3 and Figure 5. Because the stoichiometric method uses a set of chemical reactions that better represents what is occurring in the Mark-IV ER, there is more confidence in its final equilibrium composition than the non-stoichiometric method. Regardless, the purpose of the experiment was to compare the two methods of minimizing the Gibbs free energy and to determine which one would produce results that agreed with the measurements. At present and until further study shows otherwise, the stoichiometric method predicted an equilibrium composition in the initial Mark-IV ER loading that agreed with the measured composition. Future work will investigate how the electrorefiner process model handles more complex systems (e.g., the minor constituents in spent nuclear fuel and isotopes).

CONCLUSIONS

Predicting the electrorefiner inventory allows for continuing spent fuel treatment without waiting for sample analysis. To this end, an electrorefiner process model required a method to perform multi-component, multi-phase chemical equilibrium. Two chemical equilibrium methods, stoichiometric and *non-stoichiometric*, were investigated for the initial loading of the Mark-IV electrorefiner to determine which method would predict an equilibrium composition that agreed with the measured salt composition. Minimizing the Gibbs free energy using extents of reaction (the stoichiometric method) produced an equilibrium composition in the salt bath in agreement with the measured values whereas using mass balance constraints (the non-stoichiometric method) did not. Because of the geometry of the Mark-IV electrorefiner, where the metal phases are only in contact with the salt phase, the stoichiometric method can better represent the chemical reactions occurring at the phase boundaries where the non-stoichiometric method may not represent the chemical reactions occurring in the Mark-IV ER.

Table 1. Salt Sample Analysis after Oxidizing Uranium to UCl_3 Using $CdCl_2$

Sample ID	g Li (as LiCl) per 100 g Salt	g K (as KCl) per 100 g Salt	g Cd (as $CdCl_2$) per 100 g Salt	g U (as UCl_3) per 100 g Salt
SAMB20	6.0	26.1	0.01	4.26
SAMB18	6.0	26.4	No analysis	4.27
SAMB29	5.8	26.0	0.01	4.26
SAMB13	5.1	26.0	0.04	4.21
SAMB10	5.9	26.8	0.01	4.28
SAMB09	5.8	26.3	0.02	4.28
SAMB06	6.5	25.0	0.00	4.28
SAMB05	7.2	26.0	0.03	4.27
SAMB04	6.6	27.1	0.01	4.28
Average	6.1	26.2	0.01	4.27
2σ [a]	1.2	1.2	0.02	0.04

[a] 2σ = twice the standard deviation of the measured data or 95% confidence interval

Table 2. Information to Minimize Gibbs Free Energy via Non-Stoichiometric Methods

	Chemical Elements ($M = 5$) & **Z** Matrix							
Species (EA = 12)	Li	K	Cd	U	Cl	Initial Moles	μ^*_e [a]	γ_e [b]
Li (basket)	1						0	
K (basket)		1					0	
Cd (basket)			1				0	
U (basket)				1		84.08	0	
LiCl (salt)	1				1	4601.4	-82.46	0.892
KCl (salt)		1			1	3159.2	-86.63	1.655
$CdCl_2$ (salt)			1		2	126.4	-64.62	0.0662
UCl_3 (salt)				1	3		-165.6	0.169
Li (pool)	1						0	0.0018
K (pool)		1					0	5
Cd (pool)			1			4720.4	0	1
U (pool)				1			0	88.73
Total Moles (T_m)	4601.4	3159.2	4846.8	84.08	8013.4			

[a] Free energy of formation in kcal / mole for species at 773.15 K and 1 atm [11]

[b] Activity coefficients measured or estimated in molten salt and cadmium at 773.15 K [12]

Table 3. Comparison of Modeling Methods to Measured Results

	Initial Values	Final Values Stoichiometric Method	Final Values Non-stoichiometric Results	Sample Analysis (Average)	95% confidence interval
wt% Li (as LiCl)	7.04	6.95	7.0	6.1	1.2
wt% K (as KCl)	27.22	26.88	27.2	26.2	1.2
wt% Cd (as $CdCl_2$)	3.13	0.01	3.13	0.01	0.02
wt% U (as UCl_3)	0.00	4.35	0.01	4.27	0.04
wt% Li in Cd Pool	0.0	0.0	0.0	< 0.0028	NA
wt% K in Cd Pool	0.0	0.0	0.0	< 0.007	NA
wt% Cd in Cd Pool	100	100	100	100	NA
wt% U in Cd Pool	0.0	0.0	0.0	0	NA

Table 4. Stoichiometric Matrix Derived from Non-stoichiometric Formula Matrix

	Basket				**Salt**				**Cd Pool**			
Reaction	Li	K	Cd	U	LiCl	KCl	$CdCl_2$	UCl_3	Li	K	Cd	U
1	1	-1			-1	1						
2	2		-1		-2		1					
3	3			-1	-3			1				
4	-1								1			
5		-1								1		
6			-1								1	
7				-1								1

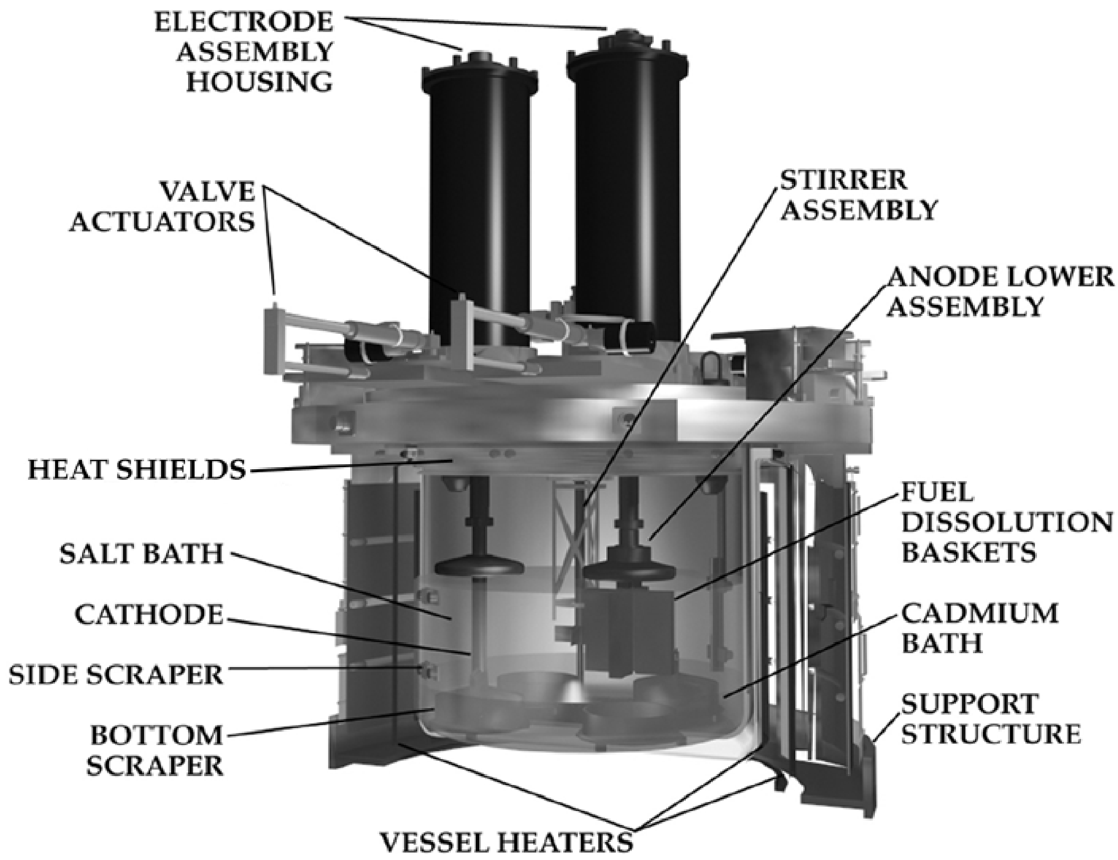

Figure 1. Mark-IV Electrorefiner

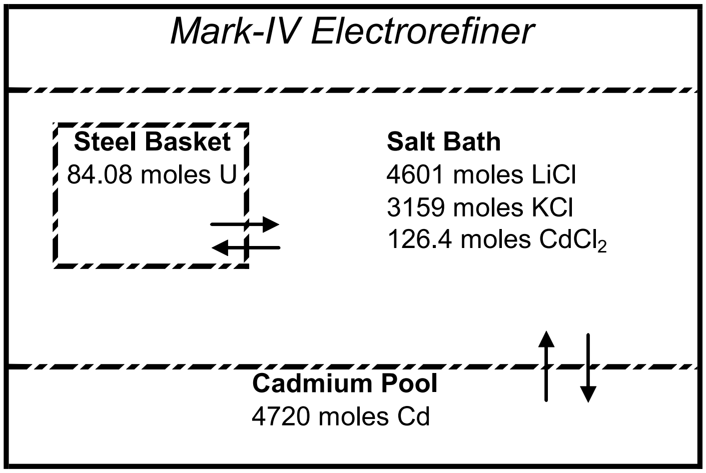

Figure 2. Schematic Showing Initial Conditions in Mark-IV Electrorefiner

$$\begin{bmatrix} \textbf{Salt - Basket Reactions} \\ 3LiCl + U_{basket} \leftrightarrow 3Li_{basket} + UCl_3 \\ 3KCl + U_{basket} \leftrightarrow 3K_{basket} + UCl_3 \\ 3CdCl_2 + 2U_{basket} \leftrightarrow 3Cd_{basket} + 2UCl_3 \end{bmatrix} \begin{bmatrix} \textbf{Salt - Cd Pool Reactions} \\ 2LiCl + Cd_{pool} \leftrightarrow 2Li_{pool} + CdCl_2 \\ 2KCl + Cd_{pool} \leftrightarrow 2K_{pool} + CdCl_2 \\ 2UCl_3 + 3Cd_{pool} \leftrightarrow 2U_{pool} + 3CdCl_2 \end{bmatrix}$$

Figure 3. Chemical Reactions at Phase Boundaries in Mark-IV Electrorefiner

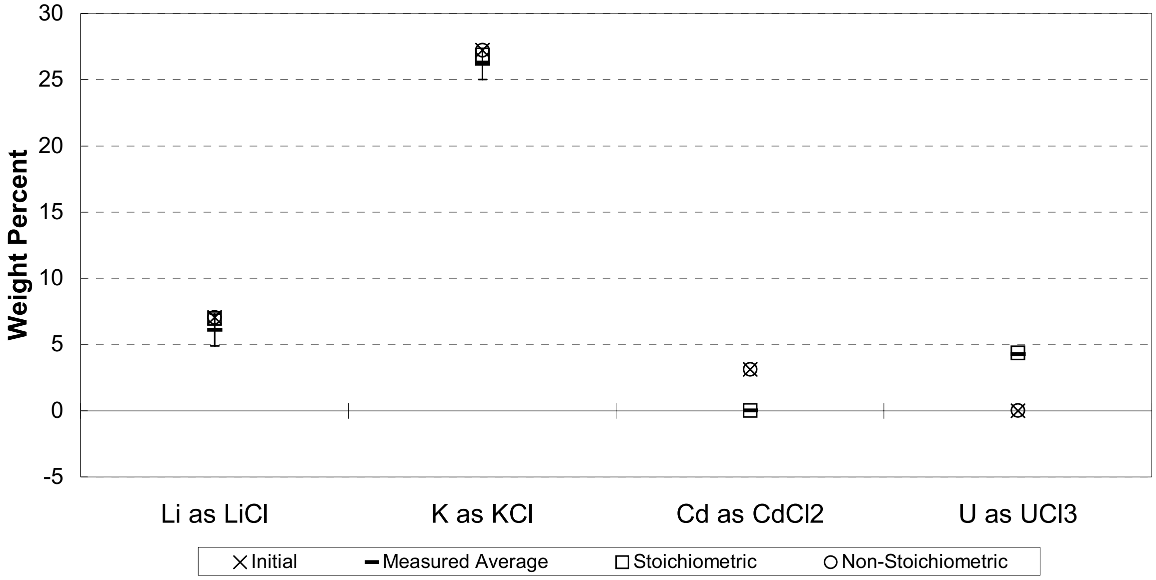

Figure 4. Measured and Predicted Mark-IV ER Composition - Initial Loading

$$\begin{bmatrix} \textbf{Salt - Basket Reactions} \\ LiCl + K_{basket} \leftrightarrow Li_{basket} + KCl \\ 2LiCl + Cd_{basket} \leftrightarrow 2Li_{basket} + CdCl_2 \\ 3LiCl + U_{basket} \leftrightarrow 3Li_{basket} + UCl_3 \end{bmatrix} \begin{bmatrix} \textbf{Basket - Pool Reactions} \\ Li_{basket} \leftrightarrow Li_{pool} \\ K_{basket} \leftrightarrow K_{pool} \\ Cd_{basket} \leftrightarrow Cd_{pool} \\ U_{basket} \leftrightarrow U_{pool} \end{bmatrix}$$

Figure 5. Independent Set of Chemical Reactions

REFERENCES

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[1] Laidler, J.J., *Pyrochemical Processing of DOE Spent Nuclear Fuel*, Proceedings of DOE Spent Nuclear Fuel – Challenges and Initiatives, Salt Lake City, Utah, December 13-16, 1994.

[2] Goff, K.M., Benedict, R.W., Johnson, S.G., Mariani, R.D., Simpson, M.F., Westphal, B.R., *Electrometallurgical Treatment Demonstration at ANL-West*, presented at American Nuclear Society Embedded Topical Meeting Spent Fuel and Fissile Material, June 2000.

[3] Smith, W.R., and Missen, R.W., 1991, *Chemical Reaction Equilibrium Analysis: Theory and Algorithms*: Malibar, Florida, Krieger Publishing Company, 364 p.

[4] Barin, I., *Thermodynamic Data of Pure Substances*, VCH, Weinheim, NY, 1992.

[5] J.M. Smith, H.C. Van Ness (1975), *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, p. 293.

[6] W.R. Smith, R.W. Missen (1982), *Chemical Reaction Equilibrium Analysis*, Wiley, p. 43.

[7] J.M. Smith, H.C. Van Ness (1975), Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, pp. 424-428.

[8] V.C. Kress, *On the Mathematics of Associated Solutions*, American Journal of Science, Volume 303, October 2003. p. 713.

[9] Microsoft Excel Solver uses the Generalized Reduced Gradient (GRG2) nonlinear optimization code developed by Leon Lasdon, University of Texas at Austin, and Allan Waren, Cleveland State University, Frontline Systems, Inc., P.O. Box 4288, Incline Village, NV 89450-4288, (702) 831-0300, Web site: http://www.frontsys.com, Electronic mail: info@frontsys.com

[10] V.C. Kress, *On the Mathematics of Associated Solutions*, American Journal of Science, Volume 303, October 2003. p. 713.

[11] Barin, I., *Thermodynamic Data of Pure Substances*, VCH, Weinheim, NY, 1992.

[12] Plambeck, J.A., *Encyclopedia of Electrochemistry of the Elements,* Volume X*,* Fused Salt Systems, Bard, A.J. (Ed), Chapter 2, Marcel Dekker, N.Y., 1976.