THERMOCHEMICAL MODEL FOR IRRADIATED ADVANCED CANDU FUEL MATERIALS

The Influence of Molybdenum on Fuel Oxidation

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Abstract

A first principles thermodynamic model for nuclear fuel is in an advanced stage of development. This model is capable of predicting the most stable phases and their proportions in CANDU fuel at varying degrees of burnup as well as predicting chemical effects associated with fuel oxidation which is a key aspect bearing on operational matters. For these reasons, the model is a useful tool to guide design and operation particularly when integrated into other computing codes that make use of thermodynamics as boundary conditions for heat and mass transfer computations.

The fuel thermochemical model is a melding of several thermodynamic projects dealing with isolated aspects of this multi-component oxide system. The model accounts for the non-stoichiometry of uranium dioxide, the solubility of dilute fission product oxides in uranium dioxide, noble metal inclusions, complex oxide phases (molybdate, zirconate, and uranate solid solutions), as well as other minor solid stoichiometric phases, and gaseous species.

To advance the model for application to Advanced CANDU Reactor (ACR) fuel, validation experiments were undertaken by controlled oxidation of mixed oxide systems simulating irradiated fuels (SIMFUEL). Emphasis was placed on the role of molybdenum (Mo) in oxidation thermodynamics. The paper includes a description of the apparatus, experimental results for uranium dioxide and SIMFUEL, and comparisons with model computations. For completeness, the principles of Gibbs energy minimization and a broad description of the fuel model are included.

## 1.	Introduction

Canada has a long and distinguished history in the nuclear industry with the achievement of the domestic and international use of the CANDU® (CANada Deuterium Uranium) reactor. The Advanced CANDU Reactor (ACR-1000) is the next generation of this reactor concept [1].

A clear understanding of the fuel behaviour under normal and extreme conditions is important to the development of the ACR. Fuel oxidation, for example, resulting from a breach in the fuel sheathing is of interest as it can affect the thermal conductivity of the fuel. The fuel system is inherently complex because of the large number of possible fission products at concentrations that are continually increasing. Further, experimentation on irradiated fuel is intrinsically difficult. To address these challenges, a fuel thermochemical model has been developed using the technique of Gibbs energy minimization. The treatment involves a combination of published thermodynamic data for pure species, mixing models to account for the solid solution phases, and adjustments as needed to represent experimental data on high temperature phase equilibrium.

With the advent of the ACR design, there is an opportunity to use the model to predict some of the physiochemical effects associated with the increased burnup of fuel made possible by the use of low enriched uranium ACR fuel [1]. At burnups expected to be about three times that of current CANDU fuel [1], the decrease in the oxygen to metal atom (where metal represents both uranium and fission product atoms) ratio in ACR fuel will be lower than past experience. Since the finite supply of oxygen (for non-defected fuel) must be shared among metallic atoms at progressively greater concentrations, the reduced O/M ratio could alter the types of minor phases as well as the proportions which may appear in ACR fuel. In principle, the resultant minor phase formation of irradiated ACR fuel can be forecast by the fuel thermochemical model which was part of the justification for its development. To add confidence to this approach, a review of the model parameters has been undertaken. Furthermore, as a test of the treatment, fuel oxidation experiments under carefully controlled conditions have been performed. This work has involved oxide mixtures prepared by sintering to simulate partial burned fuel (SIMFUEL). The emphasis in the experiments has been to better understand the role of molybdenum (Mo).

## 2.	The Thermochemical Fuel Model

### 2.1	Uranium Oxygen Binary System

The U-O binary system is shown in Figure 1. This diagram is entirely described by Gibbs energy equations for the various stoichiometric phases and solid and liquid solutions. This means that it is possible to give consideration to such matters as the thermodynamics of reaction with H_2O (or D_2O) simply by introducing the data for H_2O (or D_2O) and H_2 (or D_2) into a Gibbs energy minimization computation. Equivalently,

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the oxygen partial pressure conferred by an H_2O/H_2 proportion may be used by invoking the equilibrium constant for

$$H_2 + 0.5O_2 = H_2O \qquad (1)$$

The fuel thermochemical model has in effect knowledge of the relationship between partial oxygen pressure, O/U ratio in UO_{2+x} and temperature necessary for the computation of Figure 1.
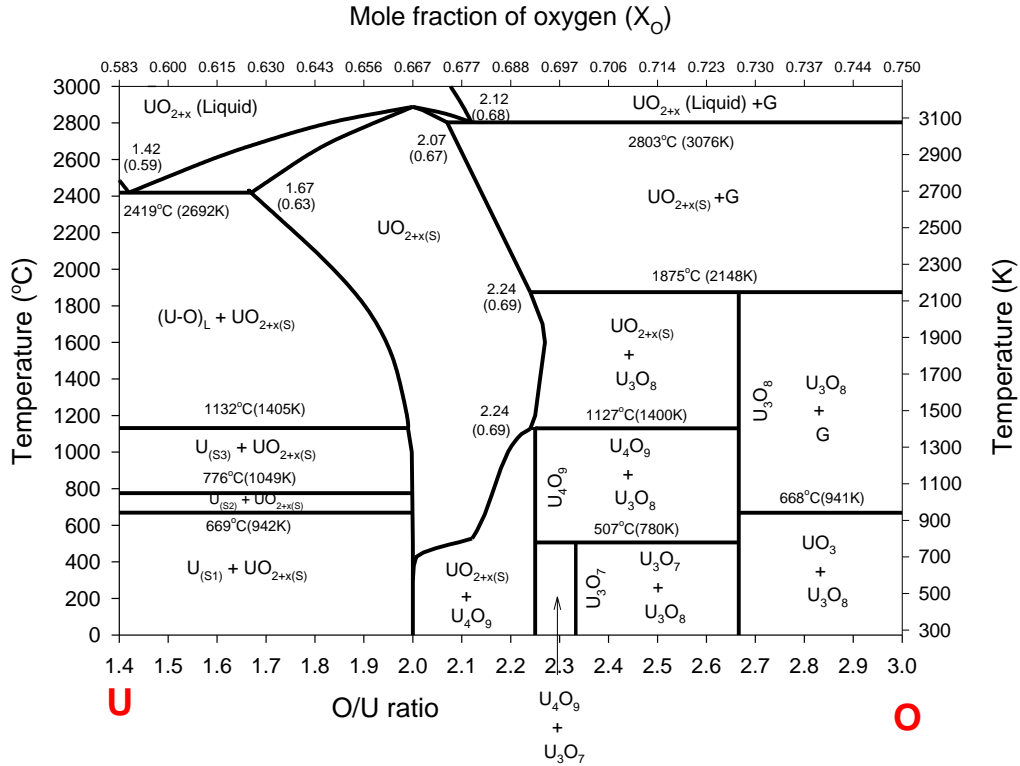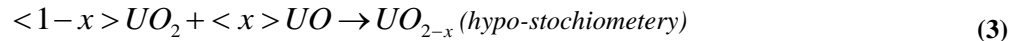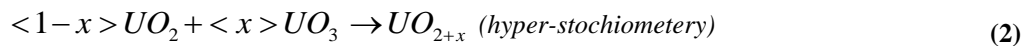

Figure 1. U-O binary phase diagram [2].

As discussed by Lewis and Thompson [2] the non-stochiometery of UO_2 in the solid and liquid phases can described as the dissolution of UO_3 or UO solute oxides in the UO_2 phase. The case of hyper-stoichiometry (UO_{2+x}, where $x > 0$) may be described by the dissolution of UO_3 in UO_2. The case of hypo-stoichiometry (UO_{2-x}, where $x > 0$) is described by the dissolution of UO. Equations 2 and 3 below indicate the equivalence of mole fractions of solute oxides and degrees of hyper- or hypo-stoichiometry.

$$<1-x>UO_2 + <x>UO_3 \rightarrow UO_{2+x} \ \textit{(hyper-stochiometery)} \qquad (2)$$

$$<1-x>UO_2 + <x>UO \rightarrow UO_{2-x} \ \textit{(hypo-stoichiometry)} \qquad (3)$$

2.2   Fission Products

To extend the power of the thermochemical model, important fission product (fp) elements have been introduced into the foundation treatment evident in Figure 1. The concentration of these "fp" elements at varying degrees of burnup is predictable by such codes as SCALES 5 [3]. With this information, it is possible with the fuel thermochemical model to predict conditions (burnup and temperature) which may give rise to new phases. These phases in the current version of the fuel model include:

- a gas phase,
- a possibly non-stoichiometric uranium dioxide matrix phase with soluble fission products,
- complex oxide precipitate phase(s) or gray phase(s),
- noble metal or white phase(s).

Background information for each of these phases has been provided in previous publications [2,4-12]. As well as leading to possibly new phases, the elements associated with fission generally have grossly different thermochemical behaviour also captured as a consequence of this thermochemical modelling approach. These chemical differences have significant effects on matters such as fission product speciation and fuel oxidation but also on many other issues involved in fuel chemistry.

3.   Gibbs Energy Minimization

The calculation of fuel phase equilibrium involves distributing oxygen among the remaining elements and calculating the Gibbs energy change from an initial condition where the elements are imagined to be chemically separate. Successive redistributions are made in a systematic manner until the Gibbs energy change can be made no more negative [13]. The result of a typical computation is given in Figure 2 for a SIMFUEL [14] sample with an oxide composition approximately representative of irradiated CANDU fuel. The small number of moles of elements corresponds to a sample with a mass of approximately 1500 mg. At a given oxygen partial pressure and temperature, the phase(s) and their respective proportions can be calculated by applying the model. As shown in Figure 2 for the sample exposed to an oxygen partial pressure of 0.614E-12 atm and temperature of 1173 K, the model predicts that 0.258E-04 mols of oxygen gas (O_2) is acquired by the SIMFUEL, and concurrently five distinct phases form. The phases and respective number of moles of each are listed below.

1. 0.10176E-04 mols of face-centered cubic noble metal solid phase
2. 0.47781E-05 mols of the hexagonal close-packed noble metal solid phase
3. 0.18138E-06 mols of strontium-barium uranate solid phase (($Sr/Ba)UO_4$)
4. 0.56993E-02 mols $UO_{2\pm x}$ solid phase with dilute fission products
5. 0.62709E-09 mols of the $Cs_2Zr_3O_7$ solid

[Fuel sample with selected fission products (in mols)]
<0.56849E-02> U + <0.11667E-06> Zr + <0.14263E-04> Mo + <0.75956E-07> Ce + <0.42121E-05> Ru + <0.86762E-07> Sr + <0.99634E-07> Ba + <0.38310E-07> La + <0.18974E-06> Nd + <0.10003E-04> Pd + <0.73875E-06> Rh + <0.12584E-08> Cs + **<0.5682E-02>** O_2 +

[amount of O_2 added to create an oxygen partial pressure of 0.61414E-12 atm]   **<0.2580E-04 >** O_2 =

[Molar amounts and fraction of the phases present]

0.00000   mol   (0.47798E-08 Cs_2MoO_4
                 + 0.42263E-08   Cs
                 + 0.40786E-10   Pd
                 + **0.61414E-12 O_2** ⟶ *Oxygen partial pressure*
                 ...
                 + 0.92932E-19 Cs_2O)
                 (**1173.15 K**, 1 atm, Ideal Gas, a=0.90477E-08)

Amount of O_2 absorbed by the sample

+ 0.10176E-04 mol   (0.91797   Pd
                     + 0.71142E-01   Ru
                     + 0.10883E-01   Rh
                     + 0.14377E-06   Mo
                     (Face Centered Cubic Noble Metal, Solid)

+ 0.47781E-05 mol   (0.73003   Ru
                     + 0.13853   Pd
                     + 0.13143   Rh
                     + 0.18070E-06   Mo)
                     (Hexagonal Close Packed Noble Metal, Solid)

+ 0.18138E-06 mol   (0.54930 $BaUO_4$
                     + 0.45070 $SrUO_4$)
                     ((Sr/Ba)UO_4, Solid)

+ **0.56993E-02 mol**   (0.99460 UO_2
                     + **0.28396E-02   'UO₃' = x**   ≈ $UO_{2.003}$
                     + **0.25026E-02   MoO₂**
                     + 0.20141E-04 ZrO_2
                     + 0.16646E-04 Nd_2O_3
                     + 0.13197E-04 CeO_2
                     + 0.33609E-05 La_2O_3
                     + 0.87977E-06   SrO
                     + 0.64937E-07 Ce_2O_3
                     + 0.36956E-09 Cs_2O
                     + 0.30322E-09   BaO
                     + 0.40677E-16   UO)
                     (Solid with UO$_{2\pm x}$ Dilute Fission Products)

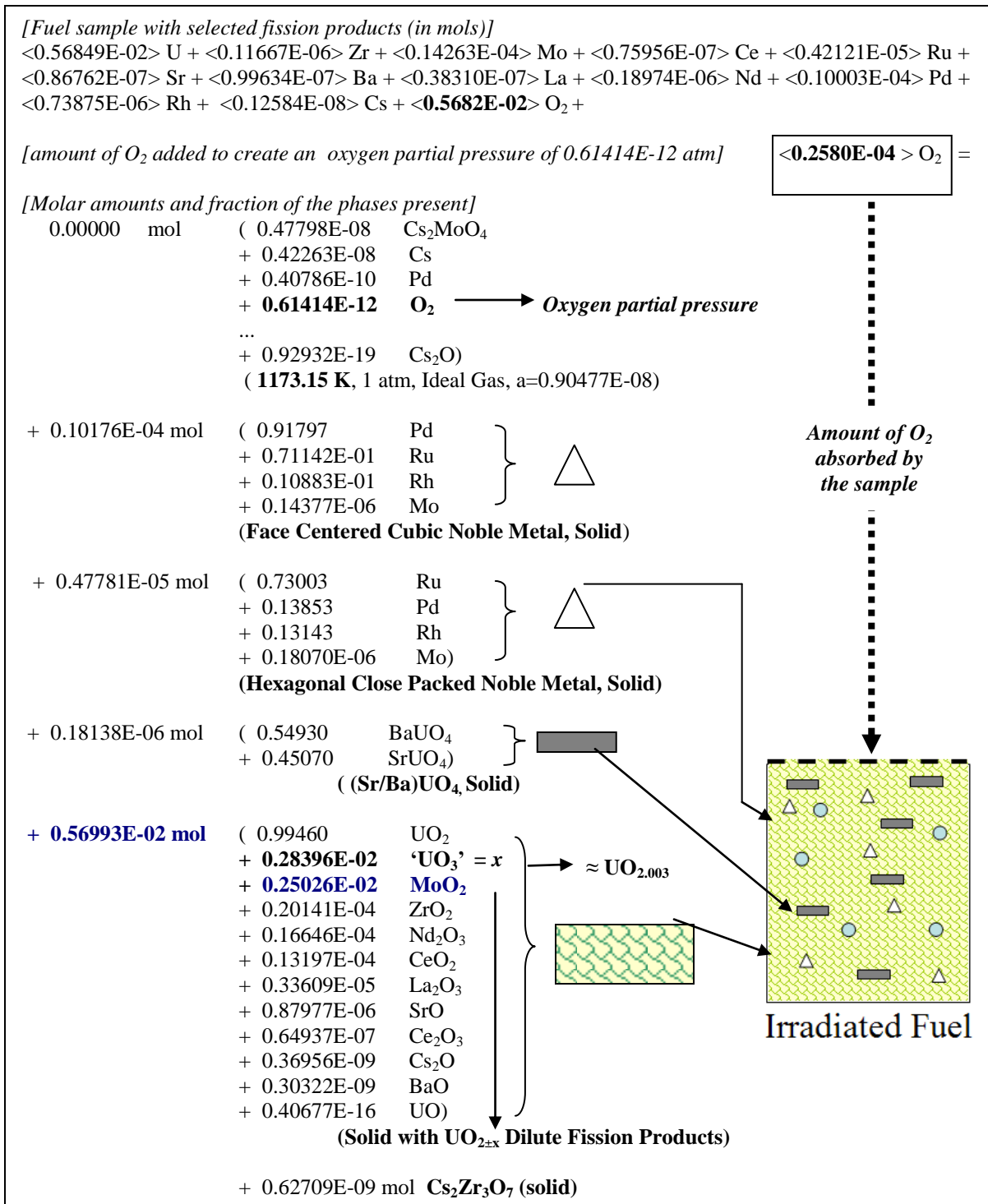+ 0.62709E-09 mol **$Cs_2Zr_3O_7$ (solid)**

Irradiated Fuel

Figure 2 Predicted phase and phase proportions for SIMFUEL at 1173 K, 1 atm exposed to an oxygen partial pressure of 0.61414E-12 atm. For practical purposes, discussed below, this oxygen partial pressure is achieved by argon gas mixtures with a specified hydrogen to water vapour ratio.

The concentrations of the components (mole fractions) in each phase are listed vertically in Figure 2. Consider MoO_2 in the $UO_{2\pm x}$ solid phase. Given the number of moles of the $UO_{2\pm x}$ solid phase (0.570E-02 mol) and the molar proportion of MoO_2 (0.250E-02 mol %), there are 0.143E-04 mols of MoO_2 in the $UO_{2\pm x}$ solid phase. This represents virtually the entire Mo inventory. The Mo in the noble metal phase inclusions is negligible by comparison for this oxygen partial pressure. The mole fraction of UO_3 dissolved in the $UO_{2\pm x}$ solid phase provides an indication of the change in stoichiometry for uranium dioxide in the presence of fission product oxides. Since equation 2 shows that it is only for the U-O binary systems that the mole fraction of UO_3 numerically equals x in UO_{2+x}, the computation draws attention to the challenge of expressing in a meaningful way the non-stoichiometry of "UO_2" when fission products are involved.

4.   Coulometric Titration Experimentation

As illustrated Figure 2 and noted above, the model is capable of predicting the number of moles of oxygen required to create a certain oxygen partial pressure at a given temperature over a sample of known composition. This ability is exploited in testing the model using the Coulometric Titration (CT) technique.

Uranium dioxide and SIMFUEL samples were oxidized at 1173 K and 1273 K under oxygen partial pressures in the range of 10^{-12} to 10^{-10} atm. SIMFUEL is ideal for this validation experimentation as it is non-radioactive and the composition is well characterized as shown in Table 1. Both SIMFUEL samples were manufactured by Atomic Energy of Canada – Chalk River Laboratories by the methods discussed in reference [14].

Table 1. Composition of SIMFUEL samples [15].

	3 at% Burnup, 4-Additives		3 at% Burnup, 11-Additives	
	ppm	±	ppm	±
Ba	9	2	1000	100
Ce	7	1	2700	300
Cs	0.11	0.03	-	-
La	3.5	0.7	900	200
Mo	900	100	180	40
Nd	18	4	4500	500
Pd	700	50	260	50
Rh	50	20	50	10
Ru	280	30	13	6
Sr	5	1	1600	200
U	890000	40	880000	40
Zr	7	1	2200	200

The CT apparatus shown in Figure 3 electrometrically converts some of the hydrogen in an argon-hydrogen mixture to water vapour using a solid oxide electrolyte (not unlike a high temperature fuel cell) [4,6,16]. The partial oxygen pressure in the argon-hydrogen-water vapour gas mixture is detected in a similar solid oxide cell (oxygen probe) from its open circuit voltage. The prepared gas mixture, with a known oxygen partial pressure, then passes over the heated uranium dioxide or SIMFUEL sample. The extent to which the sample oxidizes as it reacts with the H_2O vapour (thereby producing hydrogen) is monitored in a downstream electrochemical cell that coulometrically converts all the hydrogen to water vapour. Virtually complete conversion is assured using another open circuit solid state cell. A feedback loop from the downstream open circuit cell (oxygen probe) uses a potentiostat to regulate the current or "coulometrically titrate" the excess hydrogen with oxygen. The time integrated current associated with the "titration" provides a measure of the oxygen acquired by the sample by exposure to the known oxygen partial pressure.
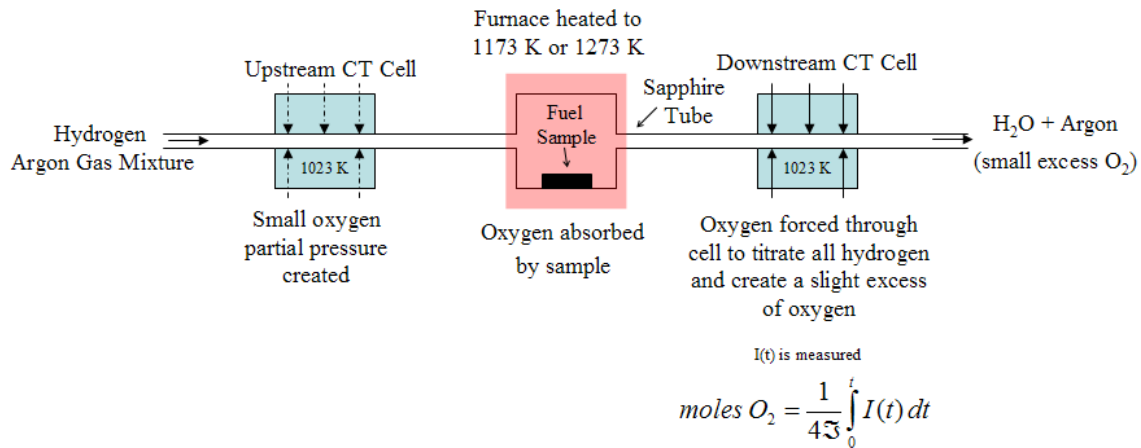

Figure 3. Schematic diagram of Coulometric Titration (CT) apparatus [4,6,16].

Although the relationship between oxygen partial pressure and oxidation (x) of pure UO_{2+x} is well known, this matter is disturbed by the presence of fission product elements which generally have vastly different abilities to combine with oxygen. Since it is the oxygen combined in water that is the source of oxygen for in-reactor defective fuel oxidation, it is the relative stability of H_2O to that of an oxide that is especially significant. This relationship is shown in Figure 4 which depicts (in the style of Ellingham) the Gibbs energy of formation of H_2O and MoO_2. Expressing the Gibbs energy of formation for both compounds on a mole of O_2 basis facilitates comparison.
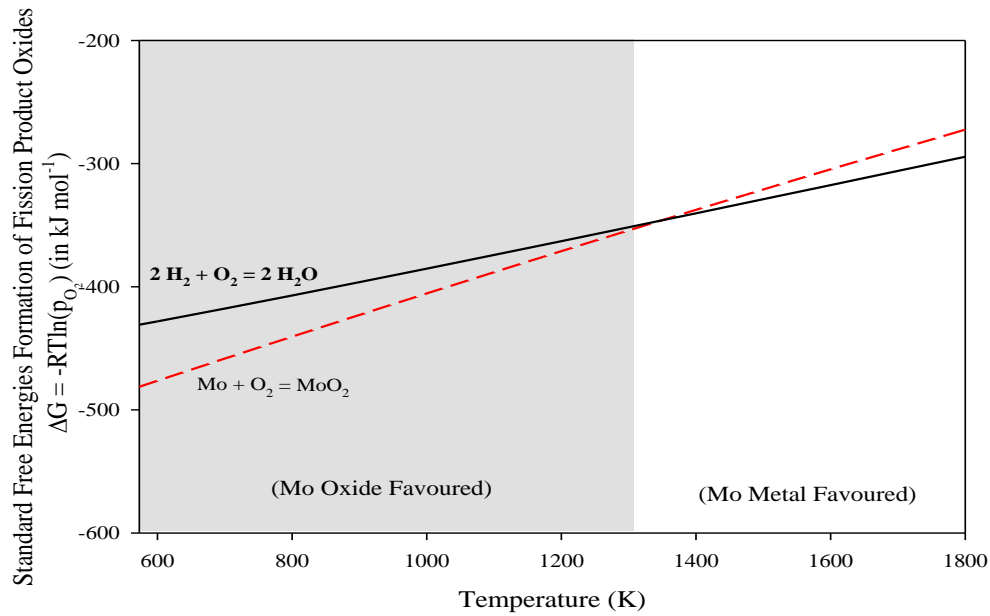
Figure 4. Ellingham Diagram comparing H_2O and MoO_2. The position of the H_2O/H_2 line applies to a ratio of 1:1; the line shifts upward when the H_2O/H_2 ratio is increased.

Other oxides not shown in Figure 4, such as PdO, lie far above the H_2O line and therefore do not easily oxidize but tend to exist in oxidized fuel as metal; UO_2 and the rare earth oxides on the other hand lie very far below the H_2O line and are very stable as oxides when in contact with H_2O. Oxidation measurements, under carefully controlled conditions, therefore provide a particularly good test for the nuclear fuel model outlined above and put a strong focus on molybdenum. This experimental approach is clearly only one of many that could be used to identify potential improvements or contribute to the validation of the thermodynamic fuel treatment. However, this experiment is of direct value to the testing of the fuel thermochemical model in relation to its use in fuel oxidation computations pertinent to a sheathing breach.

The results for the CT experimentation of uranium dioxide and SIMFUEL oxidation are summarized in Table 2.

Table 2. Summary of coulometric titration results for oxidation of uranium dioxide and SIMFUEL samples.

Sample Type	Sample Mass (mg)	Sample Temperature (K)	Oxygen Partial Pressure Over Sample (atm)	Amount of oxygen absorbed (x 10^{-5} mol)
Natural UO_2	1431.05 ± 0.05	1273 ± 1	$0.33E\text{-}10 \pm 0.03E\text{-}10$	1.9 ± 0.2
SIMFUEL, 4-additive[*]	1520.42 ± 0.05	1173 ± 1	$0.61E\text{-}12 \pm 0.06E\text{-}12$	4.4 ± 0.6
SIMFUEL, 4-additive[*]	1520.42 ± 0.05	1273 ± 1	$0.34E\text{-}10 \pm 0.03E\text{-}10$	5.6 ± 1.0
SIMFUEL, 11-additive[*]	1605.06 ± 0.05	1172 ± 1	$0.62E\text{-}12 \pm 0.06E\text{-}12$	4.0 ± 0.8
SIMFUEL, 11-additive[*]	1605.06 ± 0.05	1274 ± 1	$0.34E\text{-}10 \pm 0.03E\text{-}10$	4.6 ± 1.5

5.   Comparison of Experimental Results and Model Computations

With respect to an initial condition created by first reducing the sample in an argon-hydrogen mixture, the number of moles of oxygen acquired by a sample at a given oxygen partial pressure and temperature can be calculated using the model. The number of moles of oxygen predicted to be acquired by the sample using the original fuel model is compared to the CT measurements in Table 3. As a baseline, the expected amount of oxygen absorbed by the natural uranium dioxide sample (no simulated fission products) was studied. The model - measurement comparison is within the uncertainty range of the CT equipment. However, the model predictions for the 4- and 11- additive SIMFUEL samples were well outside of the uncertainty range of measurements.

Table 3. Comparison of Original Model to CT results.

Run Identification	Measured amount of oxygen gas absorbed (x 10^{-5} mol)	Predicted amount of oxygen gas absorbed by original U-O-fp model (x 10^{-5} mol)
UO_2 (1273 K)	1.9 ± 0.2	1.9
SIMFUEL, 4-additive[*] (1173 K)	4.4 ± 0.6	1.5
SIMFUEL, 4-additive[*] (1273 K)	5.6 ± 1.0	2.3
SIMFUEL, 11-additive[*] (1173 K)	4.0 ± 0.8	2.7
SIMFUEL, 11-additive[*] (1273 K)	4.6 ± 1.5	3.0

6.   Model Revision – $UMoO_6$

The concentration of molybdenum in the SIMFUEL samples (Table 1) and ability of molybdenum to exist as a metal (Mo) or oxide (MoO_2) as illustrated in Figure 4 was a significant clue in directing the revision of the model.

After careful investigation of the model parameters and examination of data from the open literature, the model was updated by the addition of a $UMoO_6$ [17,18] phase and modification to the solubility of MoO_2 in the $UO_{2\pm x}$ solid solution. The quantity of

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[*] See Table 1 for sample composition.

oxygen acquired by the sample was then recalculated. A comparison of the revised model and CT results is listed in Table 4.

Table 4. Comparison of Revised Fuel Model to CT results.

Run Identification	Measured amount of oxygen absorbed ($\times 10^{-5}$ mol)	Predicted amount of oxygen absorbed by updated U-O-fp model ($\times 10^{-5}$ mol)
UO_2 (1273 K)	1.9 ± 0.2	1.9 ± 0.1
SIMFUEL, 4-additive[*] (1173 K)	4.4 ± 0.6	4.2 ± 0.3
SIMFUEL, 4-additive[*] (1273 K)	5.6 ± 1.0	5.2 ± 0.4
SIMFUEL, 11-additive[*] (1173 K)	4.0 ± 0.8	3.3 ± 0.4
SIMFUEL, 11-additive[*] (1273 K)	4.6 ± 1.5	3.4 ± 0.3

As shown in Table 4, the reduction in MoO_2 solubility in UO_2, and the introduction of $UMoO_6$ have significantly affected the calculated number of moles of oxygen acquired by the samples. With these changes, both the 4- and 11-additive SIMFUELs fall within the uncertainty range of the measurements.

7.   Concluding Summary

The fuel thermochemical model is a powerful tool that has many applications in the design and operation of nuclear fuel as well as other investigations requiring a knowledge of fuel chemistry. Improvements to the model for application to ACR fuel have been discussed in relation to experimentation and places emphasis on the role of molybdenum on fuel oxidation caused by exposure to water vapour at high temperature. Currently the treatment is being readied for insertion into other computing codes that will be able to call directly the Gibbs energy minimization routine and the related database.

References

1.   Atomic Energy of Canada Limited, Advanced ACR-1000 Technical Summary, website at: http://www.aecl.ca/Reactors/ACR-1000.htm, (2007).

2.   B.J. Lewis, W.T. Thompson, F. Akbari, D.M. Thompson, C. Thurgood, and J.D. Higgs, Thermodynamic and kinetic modelling of fuel oxidation behaviour in operating defective fuel, Journal of Nuclear Materials 328 (2004) 180-196.

3.   Oak Ridge National Laboratories, SCALES-5 software, (2007).

4.   E.C. Corcoran, M.H. Kaye, F. Akbari, J.D. Higgs, B.J. Lewis, W.T. Thompson, First principles CANDU fuel model and validation experimentation. Proceedings in: 2007 International LWR Fuel Performance Meeting, San Francisco, CA, Sept. 30 – Oct. 3, 2007.

5.   M.H. Kaye, C. Morrison, J.D. Higgs, F. Akbari, B.J. Lewis, W.T. Thompson, First principles model of CANDU fuel phase equilibrium, Proceedings in: 9th International Conference on CANDU Fuel, Belleville ON, Sept 18-21, 2005.

6.   W.T. Thompson, B.J. Lewis, E.C. Corcoran, M.H. Kaye, S.J. White, F. Akbari, J.D. Higgs, D.M. Thompson, T.M. Besmann, S.C. Vogel. Thermodynamic model for uranium dioxide based nuclear fuel. International Journal of Material Research (IJMR / Z. Metallkd.) 98 (2007) 1004-1011.

7.   M.H. Kaye, A Thermodynamic model for noble metal alloy inclusions in nuclear fuel rods and application to the study of loss-of-coolant accidents, Doctoral Thesis, Queen's University, (2001).

8.   M.H. Kaye, B.J. Lewis, W.T. Thompson, Thermodynamic treatment of noble metal fission products in nuclear fuel, Journal of Nuclear Materials 366 (2007) 8-27.

9.   S. White, S. Vogel, M.H. Kaye, B.J. Lewis, W.T. Thompson, Thermodynamic modelling of the U-Dy-O System, Proceedings in: 9th International Conference on CANDU Fuel, Belleville ON, Sept 18-21, 2005.

10.   S. White, Phase equilibrium in nuclear fuel containing dysprosium, Master's Thesis, Royal Military College of Canada, (2006).

11.   J.D. Higgs, B.J. Lewis, W.T. Thompson, Z. He, A conceptual model for the fuel oxidation of defective fuel, Journal of Nuclear Materials 366 (2007) 99-128.

12. F. Akbari, M.J. Welland, B.J. Lewis, and W.T. Thompson, Considerations in modelling the melting of fuel containing fission products and solute oxides, Proceedings in: 9th International Conference on CANDU Fuel, Belleville, Ontario, Oct. 18-21, (2005).

13. C.W. Bale, A.D. Pelton, and W.T. Thompson. Facility for the analysis of chemical thermodynamics - user manual 2.1, Ecole Polytechnique de Montreal/ McGill University, (1996).

14. P.G. Lucuta, R.A. Verrall, H. Matzke, B.J. Palmer, Microstructural features of SIMFUEL- simulated high-burn-up UO_2-based nuclear fuel, Journal of Nuclear Materials 178 (1991) 48-60.

15. Private Communication, J. Mouris, ACEL-CRL, March 1, 2007.

16. R.A. Verrall, Z. He, J. Mouris, Characterization of fuel oxidation in rods with clad-holes, Journal of Nuclear Materials 344 (2005) 240–245.

17. S. Dash, K. Jayanthi, Z. Singh, N.D. Dahale, S. C. Parida, V.S. Iyer, Calorimetric studies on uranium molybdate, Journal of Alloys and Compounds 296 (2000) 166-169.

18. S. R. Dharwadkar, Standard free energy of formation of $UMoO_6$ by thermogravimetry 5 (1986) 1003-1006.