



Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

An overview of thermochemical modelling of CANDU fuel and applications to the nuclear industry

E.C. Corcoran^a, M.H. Kaye^{b,*}, M.H.A. Piro^c^a Department of Chemistry and Chemical Engineering, Royal Military College of Canada, PO Box 17000, Station Forces Kingston, ON, Canada K7K 7B4^b Faculty of Energy Systems and Nuclear Science, University of Ontario Institute of Technology, 2000 Simcoe Street N, Oshawa, ON, Canada L1H 7K4^c Fuel and Fuel Channel Safety Branch, Canadian Nuclear Laboratories, 286 Plant Road, Chalk River, ON, Canada K0J 1J0

ARTICLE INFO

Article history:

Received 13 January 2016

Received in revised form

20 April 2016

Accepted 22 April 2016

Available online 10 May 2016

Keywords:

Thermochemical treatment

Phase diagram modelling

FACTSage

Nuclear fuel

ABSTRACT

Thermodynamic models of complex chemical systems provide an elegant and cost effective means to predict chemical interactions of materials and to provide guidance to experimental research to minimise costs. Starting in 1995 at the Royal Military College of Canada, a thermodynamic treatment of irradiated nuclear fuel has been developed that not only describes the thermochemistry of the fuel at elevated temperatures during a potential Loss-of-Coolant Accident (LOCA), but it can also be used to help predict the oxidation environment for fresh fuel measurements, irradiated fuel behaviour, the aqueous chemistry of fuel debris in coolant, nuclear waste disposal, and other systems involving nuclear fuel. Furthermore, this treatment was supported by several experimental campaigns at the Canadian Nuclear Laboratories and the Institute of Transuranium Elements for validation purposes. This paper will trace the development of this treatment and demonstrate its current practice and future potential in the general context of performance and safety of nuclear fuel.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

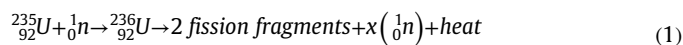
In 1995, under the initial leadership of B.J. Lewis and W.T. Thompson, a concerted effort to develop a thermodynamic treatment^{*} of nuclear fuel behaviour began at the Royal Military College of Canada (RMCC). The development of the RMCC nuclear fuel thermochemical treatment (RNFTT), which began under modest beginnings, has subsequently blossomed and has produced several journal papers [1–5], many graduate theses [6–14], numerous conference papers [15–18], other notable technical work [19,20], and, most importantly, a new generation of researchers that have begun to contribute to the field in both industry and academia. Furthermore, the nuclear fuel group at RMCC has fostered collaborations with many research groups and industrial partners both in Canada (e.g., Canadian Nuclear Laboratories (CNL), the CANDU^{®†} Owners Group, and many others) and abroad (e.g.,

Oak Ridge National Laboratories, Los Alamos National Laboratories, Sandia National Laboratories, Institute of Transuranium Elements, Commissariat à l'énergie atomique et aux énergies alternatives (CEA) Cadarache, and CEA Saclay). This manuscript gives an overview of the development of the RMCC treatment of irradiated nuclear fuel with applications of direct interest to the nuclear industry, which has been developed on the FACT/FactSage computational framework [21,22].

2. Development of a thermochemical treatment of irradiated CANDU nuclear fuel

2.1. The beginning

In a nuclear reactor, atoms of $^{235}_{92}\text{U}$ capture a thermal neutron forming $^{236}_{92}\text{U}$, which is unstable and undergoes nuclear fission, which is often written by the following reaction:



where n represents a neutron, and x can have a value of 2 or 3 [23]. The initially heavy nucleus splits into two lighter nuclei, known as fission fragments, which initially have very high kinetic energy. This kinetic energy is quickly dissipated in the fuel in the form of

* Corresponding author.

E-mail addresses: emily.corcoran@rmc.ca (E.C. Corcoran), matthew.kaye@uoit.ca (M.H. Kaye), markus.piro@cnl.ca (M.H.A. Piro).

^{*} In this paper the term “model” is used to represent a particular phase, whereas “treatment” refers to an assemblage of models that together represent a system. Thus, a model is necessarily a subset of a treatment.

[†] CANDU[®] CANadian Deuterium Uranium is a registered trademark of Atomic Energy of Canada Limited (AECL).

heat and once the fission fragments come to rest, they are then referred to as fission products. The heat from this reaction is used indirectly to generate steam and is ultimately converted to electricity via steam turbines[†]. The neutrons generated in fission, as given in Eq. (1), sustain the process. The two fission products that are produced from a single fissile atom begin to alter the chemistry of the fuel, which impacts the analysis of the burned fuel and the potential consequences during a deviation from normal operating conditions. The yield inventory of fission products represents the better part of the periodic table through a complex kinetic sequence of events involving nuclear depletion, decay, and transmutation, and their concentration changes with respect to time spent in the reactor (*i.e.*, the “burnup” of the fissile isotopes). Since the fission products have varying propensities to chemically react with oxygen in the initially pure UO_2 fuel, secondary phases may form, including gas, perovskites (that have the structure of the calcium titanium oxide compound), noble metals, *etc.* Understanding the changes in chemical reactions is commensurate to understanding changes in nuclear reactions and their inter-relationship with respect to burnup.

It is important to understand the behaviour of fission products because they can be responsible for problems within the reactor core. For example, the accumulation of fission product gases in the gap between the fuel and the sheath (cladding) affects susceptibility to fuel failure, such as iodine-induced Stress Corrosion Cracking (SCC). If the cladding were to fail, the fission products would escape to the coolant, thereby raising radiological concerns during operation. The fuel must then be removed, which can be appropriately mitigated but adds additional costs to operation. Furthermore, following a severe accident, there is a legitimate concern of fission products being released to the environment as was the case at Fukushima Daiichi and Chernobyl, which can cause health concerns with certain radioisotopes, notably iodine [24,25].

Classification of fission products based on volatility and chemical properties tends to partition the fission product elements into three or four groups. For example, based on their significant radioactive contributions in the event of a LOCA, Prussin et al. [26] classified fission products in three distinct groups:

1. Inert/Noble gases– Xe and Kr.
2. Volatiles – I, Br, Cs, Rb, Te, Se, and Sb.
3. Non-volatiles (*i.e.*, Not-so-volatile) – Ba, Sr, Mo, Tc, Ru, Rh, Pd, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Np, Pu, Zr, and Nb.

A different and more specific classification scheme based on the chemical state of the fission products has been provided by Kleykamp [27–30] and others [31]. The four classes are:

1. Fission gases and other volatile fission products – Kr, Xe, Br and I.
2. Fission products forming metallic precipitates – Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Te.
3. Fission products forming oxide precipitates – Rb, Cs, Ba, Zr, Nb, Mo, and Te.
4. Fission products dissolved as oxides in the fuel matrix – Sr, Zr, Nb, Y, La, Ce, Pr, Nd, Pm, Sm, and Eu.

It should be noted that this classification scheme places some elements (*e.g.*, Mo and Nb) in more than one category. This is due to the fact that transitions from one group to the next are based on solubility limits of the given fission products and also to changes in the chemical potential of oxygen during fuel burnup. It will be seen that one of the most important features of the RNFTT is that

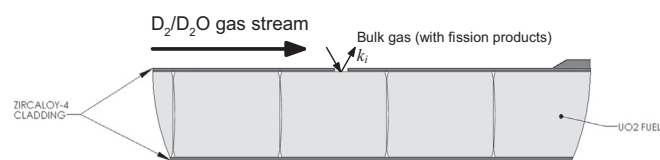


Fig. 1. A schematic diagram of a Fission Product Release Model [6].

the analysis is not limited by these classification schemes, which was the case prior to its development.

At the beginning of the development of the RNFTT, the question to be solved was what would be the source term, which describes the source of radiological release to the environment during an accident, in the unlikely event of a LOCA in a CANDU reactor[§] [32–34]. This problem was simplified to determine which chemical species would be released to the surrounding bulk gas for an oxide fuel rod, when the Zircaloy-4 cladding was breached and a gas flow of hydrogen/deuteride and steam interacted with the fuel rod at elevated temperatures. This analysis, shown in Fig. 1, became the basis for a fission product release model to support safety analyses.

Olander [35] and Cubicciotti [36–39] were early pioneers at trying to understand and predict the chemical changes occurring in the fuel as a result of irradiation. Fig. 2 depicts a conceptual representation of irradiated fuel, which illustrates some of the dominant phases.

The link between Figs. 1 and 2 is that the changes in fuel chemistry illustrated in Fig. 2 affect the chemical reactions that occur between the $\text{H}_2/\text{H}_2\text{O}$ gas flow and the inventory of the fuel (as illustrated in Fig. 1). Thus, these changes affect the transport properties (k_i in Fig. 1) of resultant species as they are released from the fuel through defects in the cladding and into the surrounding void of the fuel channel.

Initial calculations (and all subsequent ones) were performed using the FACT (now called FactSage) suite of programmes [21,22]. Specifically, the FACT compound database was expanded by an extensive literature search that added approximately 100 species to the private database. Gibbs energy minimisation calculations to compute the equilibria of the system were performed using the EQUILIB programme for various temperatures and 1 atm of hydrostatic pressure. The resulting chemical speciation and ensuing transport behaviour [1,6] were initially based on three assumptions:

1. The gas is an ideal solution phase; therefore, for each species, i , the partial pressure of that gas is equal to the mole fraction of that present multiplied by the total pressure of the system (*i.e.*, $p_i = X_{i(\text{vapour})} p_{\text{tot}}$).
2. All metallic liquids form an ideal metallic liquid solution, if they form a solution phase at all, therefore the activity of the liquid is equal to its mole fraction (*i.e.*, $a_i (\text{in liquid}) = X_i (\text{in liquid})$).
3. All solids (*i.e.*, intermetallics, oxides, and spinels) are treated as pure separate phases, in other words with a specific defined stoichiometry.

While assumption 1 is generally valid, the experimental literature is replete with examples showing that the microstructure

[§] A LOCA in a commercial CANDU reactor is classified as a Design Basis Event (likelihood estimated to be 10^{-2} to 10^{-5} years per year) – in other words an extremely rare occurrence, but for licensing and safety concerns, it is a scenario that must be considered and planned against. On December 10, 1994, Unit 2 at the Pickering Nuclear Generating Station experienced a LOCA – the only one to have ever occurred in a CANDU reactor. What is noteworthy about that event is that this reactor was functioning normally again within 6 months – the only time in industry that this has occurred. Regulatory documents 2.5.2, 2.4.1, and 2.4.2 cover this type of accident scenario.

[†] The configuration of the reactor varies with the specific type of the reactor.

the formulation stated earlier. The current treatment considers this phase as an ideal solution of UPd_3 , URh_3 , and URu_3 . Currently at the University of Ontario Institute of Technology (UOIT), a thermodynamic assessment of the U-Pd-Rh-Ru quaternary system that accounts for non-ideal behaviour is being completed [52–54] to add further refinement to the treatment.

3. Experimental work to support model development and validation

Many years of development have led to a large robust thermodynamic treatment of nuclear fuel that required experimental work to ascertain its validity and identify possible areas of improvement. Section 3.1 summarizes some of the experimental activities in regards to fuel oxidation. Sections 3.2 and 3.3 outline two follow-on investigations, conducted at RMCC and UOIT that have enhanced the RNFTT.

3.1. Coulometric titration experiments and comparison of the RNFTT

The RNFTT has been compared to experimental measurements to illustrate its capabilities for predicting fuel oxidation behaviour [12,43]. Predictions of the RNFTT were compared to measured Coulometric Titration (CT) data for fuel oxidation experiments, which measured accurately the amount of oxygen acquired by UO_2 and SIMFUEL^{††} samples exposed to various oxygen potentials [55]. The CT experimentation was performed at CNL.

The CT apparatus, which is shown in Fig. 4, is comprised of two Zirox GSM5-EL CT cells and a central sample furnace. One cell is located upstream of the sample furnace and one downstream of the sample furnace.

The Zirox GSM5-EL CT cell is composed of a ceramic tube of zirconia doped yttria with platinum electrodes on the inside and outside walls. The ceramic material conducts exclusively by O^{2-} ions making possible, by a known electrolytic current, the introduction of a known quantity of the oxygen to a gas mixture flowing through the tube. The oxygen reacts with the hydrogen to form water vapour, thereby altering the partial pressure of oxygen in the gas stream. The oxygen partial pressure altered in the CT cell can be measured using the open circuit voltage (*i.e.*, the Electromotive Force – EMF) of another solid state cell in series. A voltage feedback loop is used to control current through the CT cell to maintain a pre-specified oxygen potential.

From this study, it was concluded that the chemical interactions of molybdenum with other elements have a large impact on the oxidation behaviour of the fuel. Furthermore, these interactions are important for the accurate prediction of phase stability. Therefore, careful attention must be taken in modelling the compound oxide phases as well as the treatment of solubility of MoO_2 in the $\text{UO}_2 \pm x$ solid solution phase. These significant considerations were employed to bring the treatment predictions and measured results into better alignment with experimental measurements and have been the focus of further investigations on the ternary compound oxide phases (*e.g.*, UMoO_6) at the RMCC, as outlined below.

^{††} SIMFUEL is short for simulated fuel. It is designed to act as a replacement for real fuel in experimental work since it replicates the chemical state and microstructure of irradiated fuel by replacing radioactive isotopes of key fission products with their radioactively benign counterparts that share the same number of protons. Thus, SIMFUEL is chemically similar to irradiated fuel, without the radioactivity concerns [53].

3.2. Experimental investigation of UMoO_6

Crystallographic data can be found in the literature for over 20 ternary U-Mo-O compounds. However, only very limited thermodynamic data exists for UMoO_6 , UMoO_5 , $\beta\text{-UMo}_2\text{O}_8$, U_2MoO_8 , $\text{UMo}_7\text{O}_{22}$, and $\text{UMo}_{10}\text{O}_{32}$ [56]. Furthermore, the dominant manufacturing methods for these ternary compounds used solid-state methodologies and it is unclear if reactant impurities within the products affected the thermodynamic measurements.

To investigate these shortcomings, a novel aqueous synthesis method for UMoO_6 [57,58] was examined whereby uranyl (UO_2^{2+}) and molybdate (MoO_4^{2-}) salts were reacted in aqueous solution with subsequent precipitation, and followed by a multi-stage drying process. The U and Mo were matched in atomic proportions during the aqueous synthesis, and drying produced UMoO_6 of a high purity.

Preliminary thermodynamic studies of the high purity UMoO_6 product compound found a decomposition temperature and enthalpy of formation within the uncertainty range of comparable measurements documented in recent studies [59]. The aqueous synthesis proposed by Barry et al. [57] identified a series of unique crystal structures for the intermediate compounds resultant from drying (shown in Fig. 5) with X-Ray Diffraction (XRD) characterisation results, shown in Fig. 6 compared to those found in the literature [60,61].

It should be noted that the XRD pattern from Barry et al. [57] differs completely from the literature and the details of this are examined at length in Barry et al. [57]. However, in the case of Fedoseev et al. [61] the differences are most likely due to contamination. In the case of Juenke and Bartram [60] the method of synthesis is different. It has been determined that the pattern shown in Fig. 6 is a metastable structure of UMoO_6 , that will degenerate if exposed to temperature and then produce the pattern from Juenke and Bartram [60].

Barry et al. [57] also found that reactant contamination of products produced by solid-state manufacturing has little impact on some thermochemical measurements. Further investigation of the manufacturing process and measurement of the thermochemical properties of the other ternary compounds (*e.g.*, UMoO_5 , $\beta\text{-UMo}_2\text{O}_8$, U_2MoO_8 , $\text{UMo}_7\text{O}_{22}$, and $\text{UMo}_{10}\text{O}_3$) is underway at RMCC.

4. Integrating thermodynamic calculations in multi-physics codes for engineering applications

Many numerical investigations of nuclear fuel behaviour rely on an understanding of various thermochemical properties, such as phase equilibria, phase composition, oxygen chemical potential, and several other pertinent parameters. These investigations typically predict fuel behaviour on a continuum scale using finite element codes to simulate engineering applications related to nuclear fuel performance and safety. Multi-physics simulations typically involve solving partial differential equations representing heat and mass transport coupled with structural mechanics and sometimes lower-length scale models. Thermochemical calculations often provide – either directly or indirectly – material properties, boundary conditions, and source terms to the aforementioned simulations.

The following sub-sections provide examples of how thermochemical treatments have been used in multi-physics simulations to predict nuclear fuel behaviour to support engineering performance and safety analyses. Details are provided on what specific role(s) thermodynamic calculations play within a multi-physics framework. Three different simulations are presented, including the evolution of fuel chemistry throughout the course of

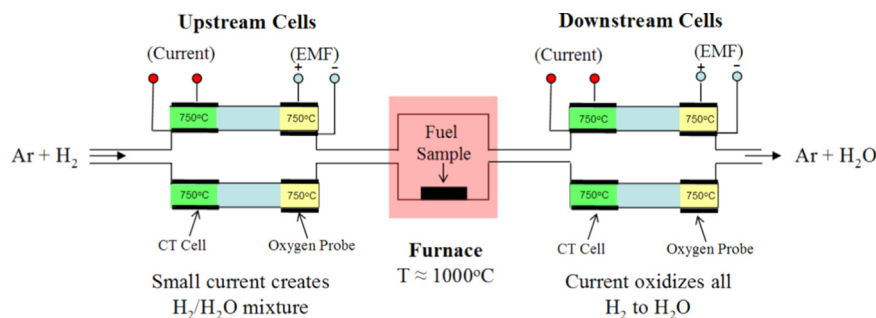


Fig. 4. Schematic diagram of the coulometric titration apparatus.

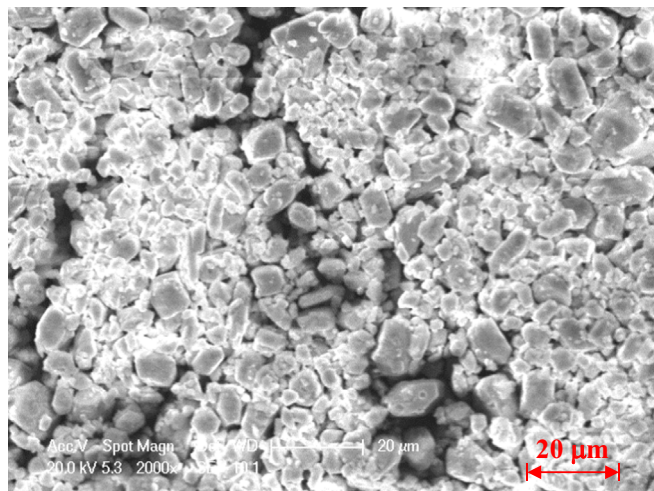


Fig. 5. SEM image of metastable UMoO_6 (labelled Compound 2 in Fig. 6) [57].

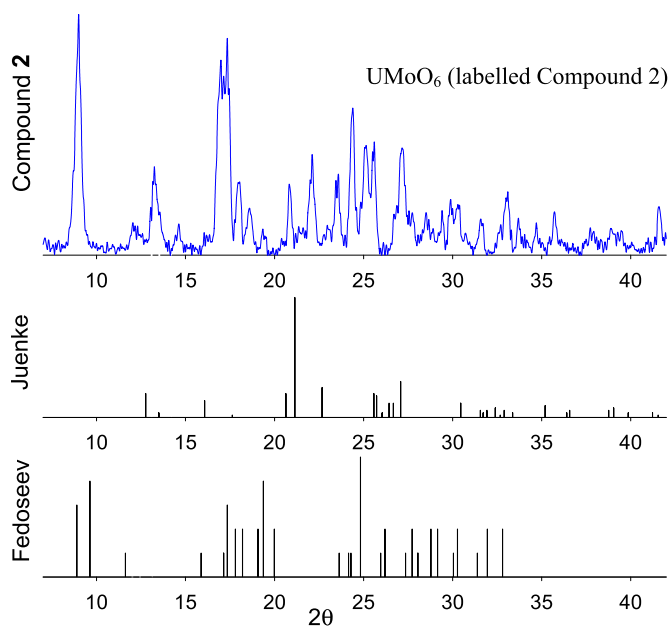


Fig. 6. Powder-XRD of metastable UMoO_6 compound (labelled Compound 2) [57], compared to that published for UMoO_6 obtained by the solid state synthesis of Juenke et al. [60] and aqueous synthesis method of Fedoseev et al. [61].

irradiation under normal operating conditions, oxidation of defective fuel under abnormal conditions, and non-congruent melting of nuclear fuel during a severe accident.

4.1. Irradiated fuel chemistry under normal operating conditions

The temporal and spatial evolution of coupled thermochemical and nuclear reactions of irradiated fuel has been simulated for the first time by Piro et al. [62]. In this work, a multi-physics framework was provided by the Advanced Multi-Physics (AMP) code [63], which coupled heat transfer calculations on a three dimensional mesh, with isotopic calculations performed with Origen-S [64] and thermochemical calculations with Thermochemica [65]. Elemental concentrations computed from nuclear physics calculations in Origen-S and temperatures computed by heat transfer calculations with AMP provide the necessary input to Gibbs energy minimisation calculations in Thermochemica^{††}. The thermodynamic treatment described in Section 2 was then used to predict phase equilibria in the fuel.

Fig. 7 illustrates a contour plot of the oxygen chemical potential in a three dimensional fuel pellet using the aforementioned computational framework. Although some conventional approaches have computed the spatially varying oxygen chemical potential in the fuel, they were limited to fresh fuel under the assumption of a single phase and were unable to capture multi-component multi-phase equilibria. This work includes the fission products and the minor phases that are formed. An advantage of being able to predict the spatially varying oxygen chemical potential is to provide it as input to oxygen transport calculations and other transport mechanisms.

In combination with predicting the chemical potentials of all the system components, this framework also predicts the formation of various phases in the fuel. Fig. 8 shows the predicted radial variation of phases that are formed in irradiated nuclear fuel, which includes a dominant fluorite oxide phase, inert gas, hexagonal closed packed noble metal phase, and several other minor phases. The radial variation of phases in Fig. 8 is due to a combination of a temperature gradient (decreases from $r/r_0=0$ to 1) and a gradient of fission product concentrations (increases from $r/r_0=0$ to 1).

An advantage of this framework is that incorporation of chemical effects on the fuel surface with the neighbouring zirconium alloy cladding (which houses the fuel) is relatively straightforward. This may be used to better understand and predict the potential for SCC to take place in the cladding, which is a very important failure mechanism that constrains operational performance and manoeuvrability. Furthermore, this approach may give credence to designing alternate mitigation strategies that may alleviate current constraints on performance, which has a direct impact on revenue during commercial operation.

^{††} The hydrostatic pressure was assumed constant at 1 atm for these simulations, which is a reasonable assumption given the known insensitivity and uncertainties associated with the overall approach.

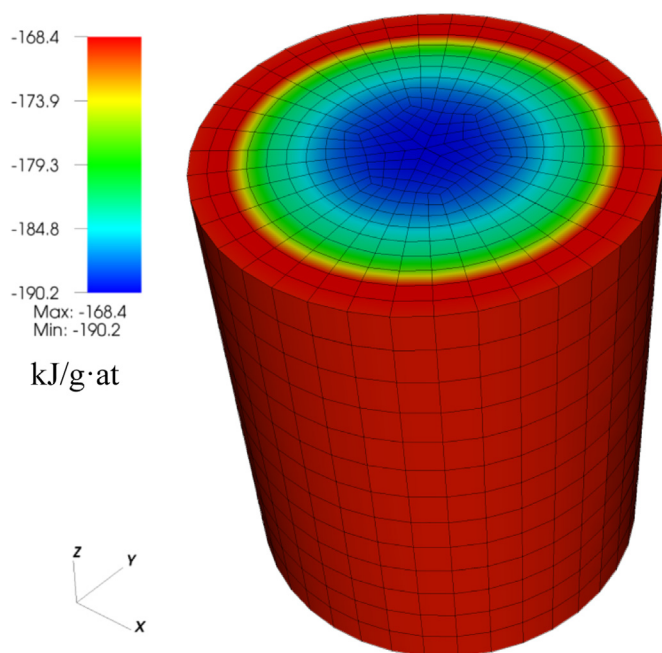


Fig. 7. A contour surface plot of the oxygen chemical potential [kJ/g at] of a three dimensional nuclear fuel pellet is shown. This calculation is based on UO_2 fuel with an initial enrichment of 3.5% ^{235}U , a constant specific power of 15 kW/kg and burnup of 30 GWd/t(U). This corresponds to a parabolic temperature profile that corresponds to a maximum of $\sim 750^\circ\text{C}$ at the centre and $\sim 285^\circ\text{C}$ on the outer surface. More details are provided by Piro and Besmann [66].

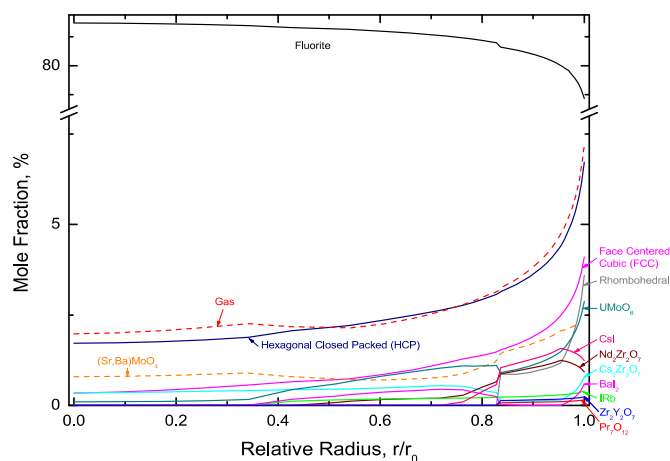


Fig. 8. The predicted radially varying distribution of phases in irradiated nuclear fuel is shown. The calculation of phase equilibria shown here includes a parabolic temperature distribution (with a maximum of $\sim 600^\circ\text{C}$ at $r/r_0=0$ and minimum of $\sim 285^\circ\text{C}$ at $r/r_0=1$) and a non-uniform distribution of 24 chemical elements (generally with a minimum at $r/r_0=0$ and maximum at $r/r_0=1$, except for U). More details are provided by Piro et al. [62].

4.2. Oxidation of defective fuel under abnormal conditions

Higgs et al. [4] showed that thermodynamic calculations have also played a supporting role in predicting the oxidation of nuclear fuel. Under abnormal conditions, the cladding that normally protects the fuel from the surrounding heavy water coolant may defect, permitting oxidation of both the fuel and the inner surface of the cladding. In addition to important mechanisms of releasing radioactive materials to the coolant (i.e., fission product gases and fuel debris), the presence of water vapour degrades heat transfer across the fuel-clad gap. Furthermore, the oxidation process itself yields a hyperstoichiometric fuel that has a lower thermal conductivity, which further increases fuel temperatures. Also,

hyperstoichiometric fuel has a lower incipient melting temperature, as shown in the phase diagram in Fig. 3 which further increases the risk of a more severe situation under defective conditions.

In the work by Higgs et al. [4], fuel oxidation simulations were performed in the COMSOL Multi-physics environment, which coupled heat transfer and solid-state diffusion of oxygen in a two dimensional axisymmetric framework. A simplified thermochemical model of UO_{2+x} provided a relationship between temperature, composition and the oxygen chemical potential. Thus, local temperature and oxygen concentrations from heat and mass transport calculations provided input to this thermochemical model, which then predicted the oxygen chemical potential that was used to drive oxygen transport through the solid fuel matrix and in the vapour phase of $\text{H}_2/\text{H}_2\text{O}$ present in the fuel cracks. Furthermore, the changes in the local fuel stoichiometry provided input to various non-linear material and physical models, such as thermal conductivity, specific heat capacity and kinetic reaction rates on the fuel surface.

Results of the aforementioned coupled numerical framework are shown in Fig. 9, which illustrates predictions of the oxygen-metal ratio of the fuel with respect to experiments that were performed at CNL. In this particular case, a defective fuel element was used with open blisters and a faulty end-cap (as identified below), which permitted water to come into contact with the fuel. Overall, thermochemical modelling of non-stoichiometric nuclear fuel played an integral role in predicting the oxidation behaviour of defective fuel.

4.3. Non-congruent melting of nuclear fuel during a severe accident

The third and final scenario that is presented that demonstrates the role of thermodynamic modelling in multi-physics applications simulates non-congruent melting of hyperstoichiometric uranium dioxide fuel. In the work of Welland et al. [67], numerical simulations were performed in the COMSOL Multi-physics platform, that coupled time dependent heat and mass transport calculations with a phase field model, as derived from the theory of irreversible processes. As previously mentioned, the initially stoichiometric UO_2 fuel may become hyperstoichiometric following a fuel defect. This reduces the thermal conductivity while also decreasing the incipient melting temperature, which together reduces the margin to fuel melting. These matters are of great importance in the context of safety analyses under upset and accident conditions.

From a numerical point of view, there are some similarities in this approach with that taken by Higgs et al. [4], whereby heat transfer and solid state diffusion calculations are closely coupled with a thermochemical representation of UO_{2+x} fuel. However, an important difference is the extension of the same thermochemical treatment to capture phase changes, which is provided by a phase field model. Together, the simulation framework is able to predict local temperatures, oxygen content and compositions of phases, which may be either solid, liquid, or an interfacial region. The overall thermochemical representation is fully self-consistent among all material behaviours.

Simulations performed by Welland et al. [67] were compared to laser-flash melting experiments that were conducted by Manara et al. [68] at the Institute for Transuranium Elements in Germany, and were generally in good agreement. In brief, these experiments heated a UO_{2+x} sample with a laser, producing a self-crucible molten pool under a high hydrostatic pressure of inert gas. The temperature was measured using a fast optical pyrometer.

A sequence of times in the experiment is shown in Fig. 10 that illustrates the changes in the local oxygen content in the fuel. The laser heats the sample from the top and is being applied during

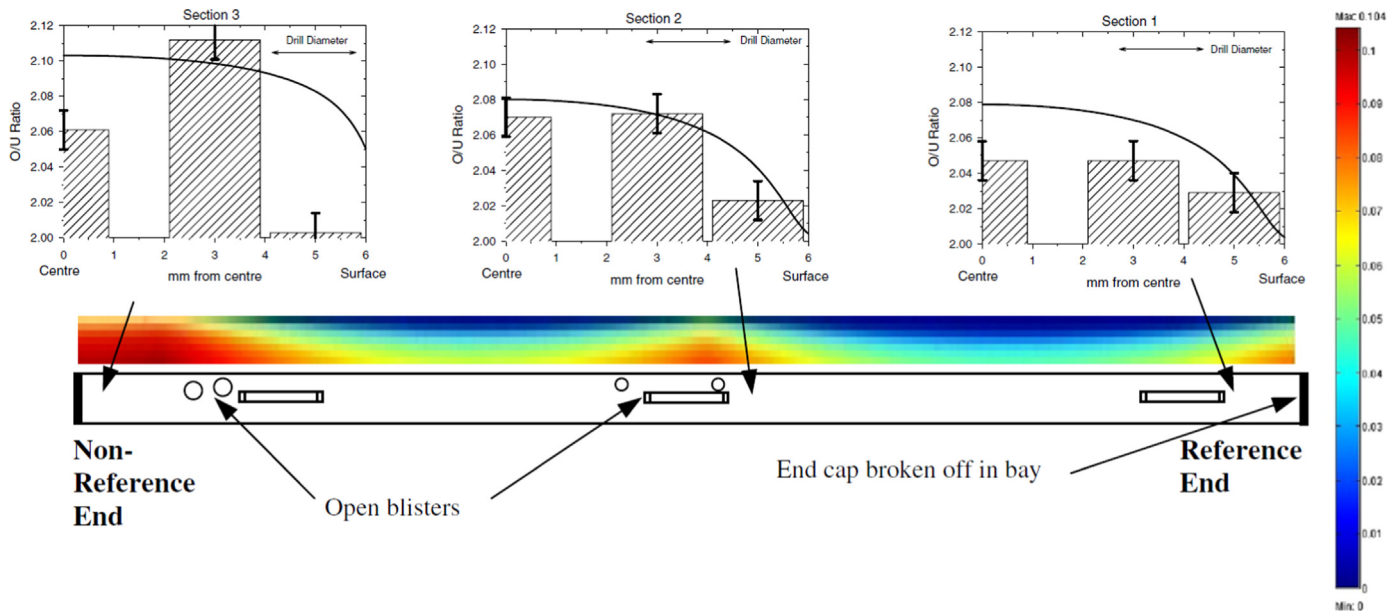


Fig. 9. Numerical predictions by Higgs et al. [4] of the oxygen–metal ratio in defective fuel are compared to oxidation experiments performed at the Chalk River Laboratories.

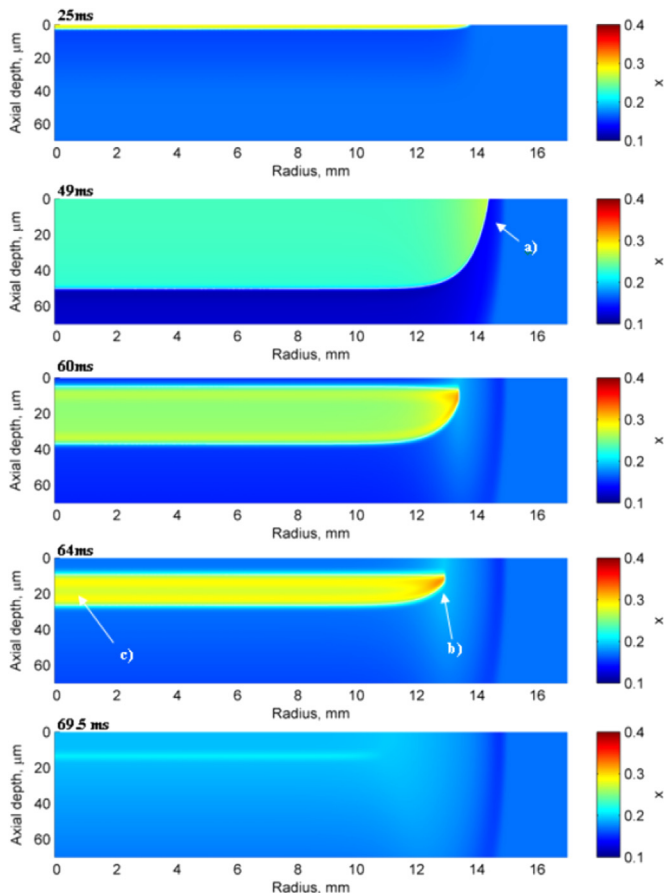


Fig. 10. Simulation results of changes in oxygen concentration at five different periods in time in initially $\text{UO}_{2.17}$ fuel. Point (a) corresponds to oxygen depletion ahead of the liquid phase, point (b) shows the local spikes in oxygen concentration due to solidification, and (c) illustrates local oxygen rich regions in the liquid due to axial solidification. Figure copied from Welland [11].

the first two time steps shown in Fig. 10. The laser power is rapidly decreased for the remaining three times. Thus, the highest temperature in the fuel is near the surface where the laser is heating the sample. Comparing the surface plots at times 25 and 49 ms,

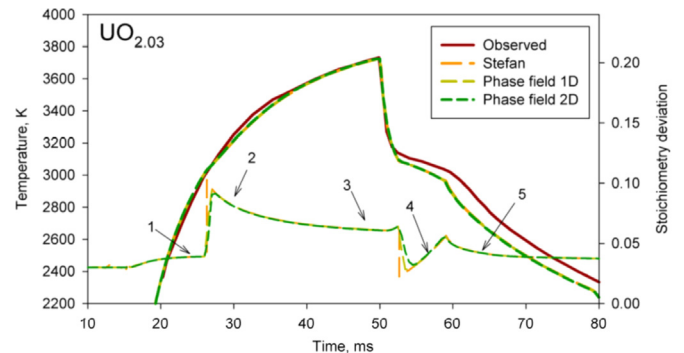


Fig. 11. Numerical predictions of surface temperature and composition of $\text{UO}_{2.03}$ fuel are compared to laser flash measurements. Figure copied from Welland [11].

oxygen has migrated up the temperature gradient under the effect of thermodiffusion.

Fig. 11 compares the predicted evolution of fuel surface temperature with pyrometry measurements throughout the course of the experiment with $\text{UO}_{2.03}$ fuel. First, the laser heats the fuel up until about 48 ms into the experiment where the power is reduced. Initially, the fuel surface is entirely solid and initially melts at about 3080 K. Upon cooling, a two phase region is found stable on the surface between about 50 and 60 ms, which then completely solidifies.

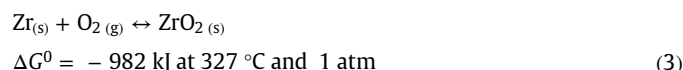
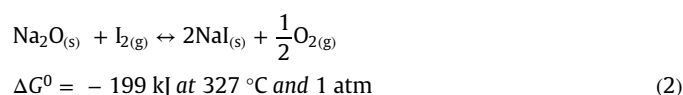
The computational framework by Welland [11] to simulate non-congruent melting of fuel is generally in good agreement with laser flash melting experiments, which gives confidence in the general approach and has important implications on safety analyses. The overall approach rests on a self-consistent representation of the thermochemistry of the fuel, which has provided material properties and boundary conditions for the multi-physics framework.

5. Current and future applications deriving from the treatment

5.1. New SCC mitigation techniques for CANDU nuclear reactor fuels

In the early 1970s, the mitigation of SCC failures of Zircaloy-4

fuel cladding in CANDU nuclear reactors resulted in the application of graphite based coatings, commonly referred to as CANLUB^{§§} [69]. Ongoing investigations are attempting to ascertain whether the chemical impurities in the CANLUB coating benefit SCC mitigation [70,71]. One potential mechanism involves the sequestering of iodine via its reaction with alkali (or alkaline earth) metal oxide impurities within the CANLUB. Simple calculations using the RMCC thermodynamic fuel treatment indicate that alkali (or alkaline earth) metal iodides (*i.e.*, NaI) within the coating may limit the overall gaseous iodine available for interaction with Zircaloy-4 cladding (Eq. (2)). Furthermore, the oxygen produced in the reaction may repair existing cracks in the protective ZrO₂ layer (Eq. (3)); the negative value of Gibbs energy of reaction (ΔG^0) indicates product-favoured reactions. Consequently, alkali (or alkaline earth) metal impurities may be advantageous in mitigating SCC where CANLUB protective cladding coatings are used.



5.2. Measuring thermodynamic properties of aqueous systems at elevated Temperatures

Assessing and evaluating thermochemical data have been an ongoing effort during the development of the RNFTT. The compound database in the FACT (and FactSage) programmes has incorporated thermochemical data from many sources (*e.g.*, the JANAF tables [72,73], Barin, Knacke, and Kubaschewski [74], Cordfunke and Konings [75], and Gurvich et al. [76], to name but a few). But, there are certain situations where the quality of the data is open to interpretation. For example, the RNFTT has also been applied to other situations than in-reactor conditions, notably to aqueous systems. One difficulty in these applications is that the thermochemical data for aqueous species is often estimated or extrapolated from room temperature data to much higher temperatures [77]. Under normal operating conditions within a reactor, the coolant is kept liquid by applying a large hydrostatic pressure (approximately 100 atm) to achieve temperatures between 250 and 300 °C. Conversely, most aqueous data are measured at 25 °C and 1 atm [72,78].

While not directly part of the RNFTT, interactions between the cladding and the fuel have long been recognised as important in influencing the chemistry of the fuel. Thus, the behaviour of the principle components of Zircaloy-4 cladding material (*i.e.*, Zr, Sn, and Nb) are of interest, and how these metals interact with the coolant at elevated temperatures and pressures. One method of examining these conditions for aqueous systems is to construct a Pourbaix diagram [79]. The case of Sn illustrates how uncertainties in the estimated data for the standard entropy, S^0 , when extrapolated to elevated temperatures, can lead to different diagrams, as shown in Fig. 12.

A study of the Sn system was performed at UOIT [80] to investigate these properties. Using the apparatus shown in Fig. 13, measurements of E_H and pH were made of a series of Sn solutions at 85 °C. The total metal concentration of the solution was determined via inductively-coupled plasma emission spectroscopy

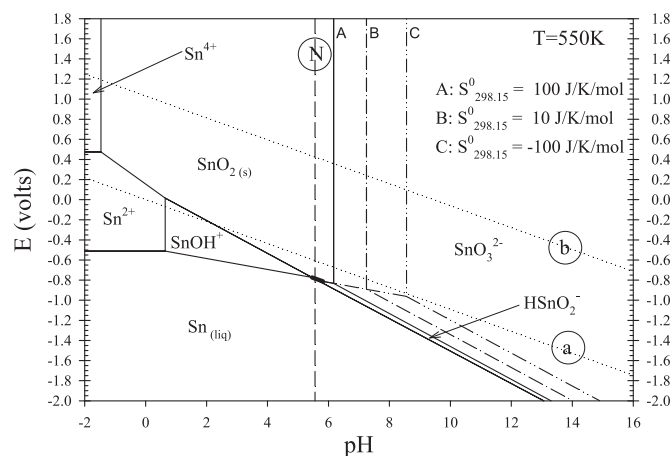


Fig. 12. The Sn Pourbaix diagram at 550 K showing the effect of varying S^0 for SnO_3^{2-} . Metallic tin is stable as a liquid. The concentration of all aqueous species is $10^{-6} \text{ mol L}^{-1}$. Note that the lines marked ⓐ and ⓑ indicate the hydrogen saturation and oxygen saturation lines, respectively. Neutral pH is indicated by the line marked Ⓝ.

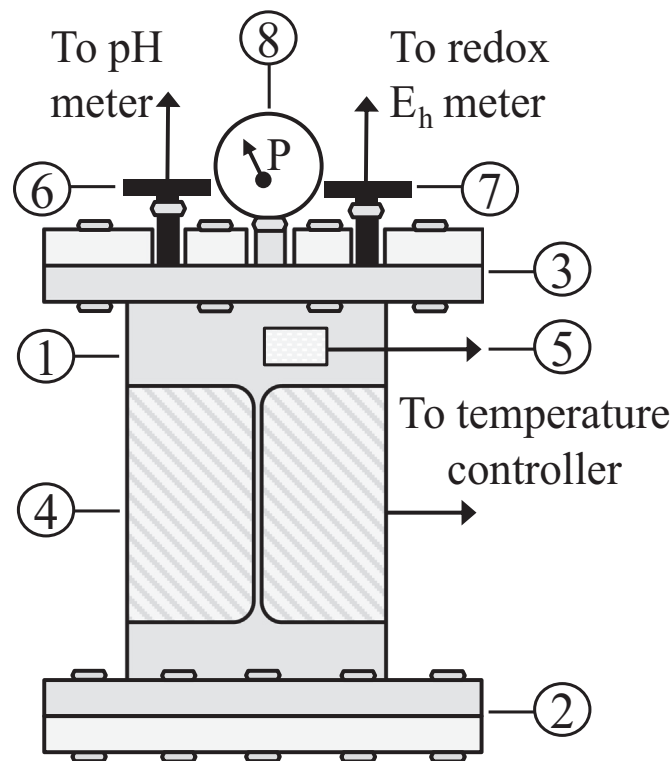


Fig. 13. Schematic diagram of the reaction vessel for elevated temperature solubility measurements. 1. Teflon-lined vessel body; 2 and 3. 316 stainless steel blind flanges; 4. band heater; 5. K-type thermocouple; 6, and 7. elevated temperature pH and ORP electrodes; 8. pressure gauge [80].

or flame atomic absorption spectroscopy depending on the range of expected concentrations. This allows direct comparison to the Pourbaix diagram.

As determined by the test electrodes, the temperature limit for the operation of the vessel shown in Fig. 13 is approximately 115 °C. Currently, a test vessel using more resistant electrodes is being designed, to push the maximum temperature upwards toward 250 °C.

5.3. Aqueous chemistry of actinoids

In the event of defective fuel, as described in Section 4.2, fuel

^{§§} CANLUB is short form for CANDU LUBricant, a proprietary graphite based material that serves as an interlayer between CANDU UO₂ fuel and the surrounding cladding.

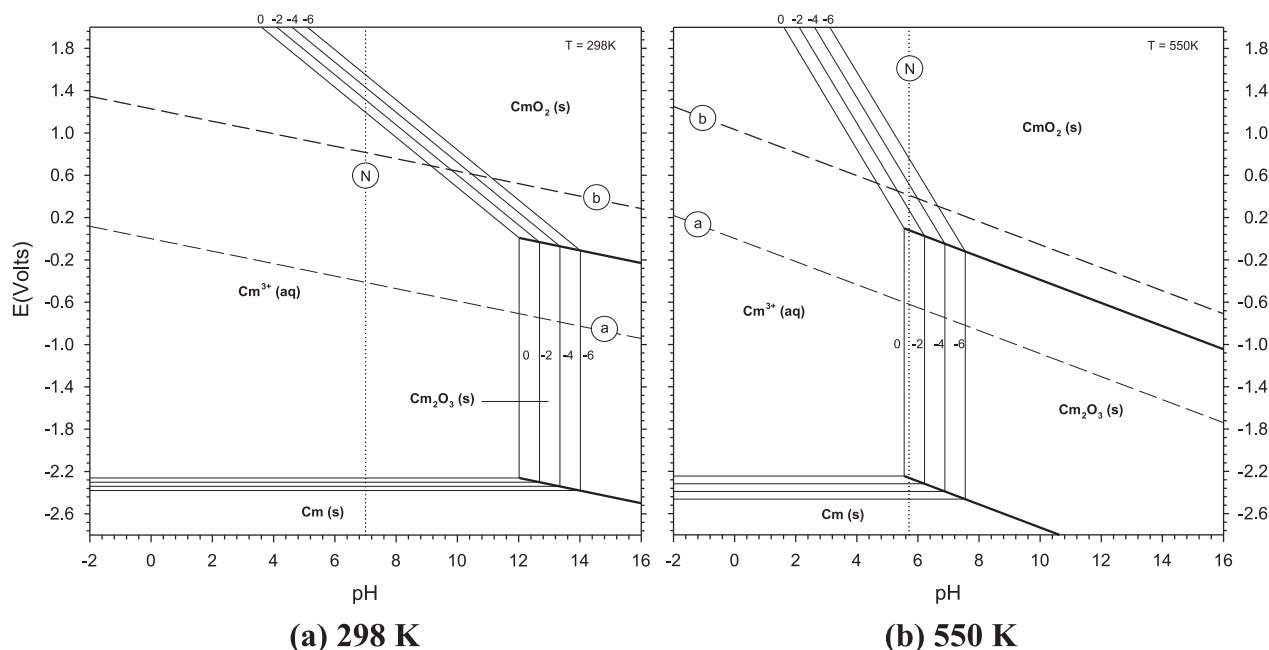


Fig. 14. Cm Pourbaix diagrams shown for 1, 10^{-2} , 10^{-4} , and 10^{-6} mol L $^{-1}$. Figure copied from Piro et al. [81] (a) 298 K (b) 550 K.

debris may be expelled from a fuel element to the surrounding coolant and circulate in the Primary Heat Transport System (PHTS). Although the quantity of uranium that is soluble in the coolant under normal conditions is less than 1 ppb [79], the same generalisation may not apply to higher atomic number actinoids – namely Neptunium, Plutonium, Americium, and Curium – that are produced via neutron activation and decay. A particular concern during maintenance or decommissioning of the PHTS is the leaching of some of these actinoids from the debris into the coolant, where they could remain trapped in irregularities (e.g., crevices) within the PHTS [81]. Therefore, when the coolant is expelled, these actinoids may not be discharged, leading to unexpected radiation exposure for workers during maintenance or decommissioning. Thus, it is important to understand the solubility of the actinoids in water in this context.

The RNFTT was used to investigate the aqueous chemistry of the (U,Np,Pu,Am,Cm – H₂O) system to better understand this behaviour. It was concluded that small quantities of Cm will dissolve in the coolant (~100 ppm, as can be seen in Fig. 14b) while the other actinoids are predominantly stable as solid oxides [81]. Moreover, these analyses demonstrated that during dryout, where the electrochemical potential and pH increase, CmO₂ precipitates [81]. This behaviour is graphically illustrated in the Cm Pourbaix diagrams shown in Fig. 14 below at 298 and 550 K, respectively.

6. Summary and future work

The development of the RNFTT, founded by Thompson and Lewis [5], has evolved over time to capture the behaviour of irradiated fuel thermochemistry that bear on many practical engineering applications. The initial impetus of its development was to better understand the chemical behaviour of radioactive fission products following an accident. Later, it evolved into a more comprehensive multi-component and multiphase treatment of irradiated nuclear fuel. Several experimental campaigns have been pursued to provide validation under various conditions. Also, the treatment as a whole and some specific sections of the treatment have been integrated into multi-physics codes to simulate various aspects of nuclear fuel performance and safety.

Finally, the RNFTT is a robust platform for the investigation of chemical stability in nuclear fuel. It has been applied to assist our understanding of fuel behaviour and has afforded a deeper insight to nuclear fuel safety and design. Other than relatively minor improvements to the RNFTT itself, the future work envisioned involves applying the model to industrial and research applications.

Acknowledgements

The authors would like to acknowledge the mentorship, supervision, and friendship of Drs. William (Bill) Thompson and Brent Lewis. Their successful partnership and collaboration created a dynamic research group that has enriched many lives. It is also a testament to the principle that the whole is greater than the sum of the parts. The authors would also like to congratulate Dr. Chris Bale on this celebration of his 70th birthday. Behind the work presented here, is another successful collaboration of Drs. Bale, Pelton, Thompson, and Eriksson in their creation of the FACT system, which evolved into FactSage, and their on-going commitment to advancing the science of applied thermodynamics.

The authors also acknowledge the many colleagues, past and present, that have contributed to this work by sharing and publishing their research. MHP thanks N. Lair (CNL) for assistance with some of the figures. Finally, thank you to the various funding agencies that have provided monetary support over the years, in particular the Natural Sciences and Engineering Research Council (NSERC) of Canada, CANDU Owner's Group, and AECL.

References

- [1] B.J. Lewis, B.J. Corse, W.T. Thompson, M.H. Kaye, F.C. Iglesias, P. Elder, R. Dickson, Z. Liu, Low-volatile fission product release and fuel volatilization during severe reactor accident conditions, *J. Nucl. Mater.* 252 (1998) 235–256.
- [2] B.J. Lewis, W.T. Thompson, F. Akbari, D.M. Thompson, C. Thurgood, J. Higgs, Thermodynamic and kinetic modelling of fuel oxidation behaviour in operating defective fuel, *J. Nucl. Mater.* 328 (2004) 180–196.
- [3] M.H. Kaye, B.J. Lewis, W.T. Thompson, Thermodynamic treatment of noble metal fission products in nuclear fuel, *J. Nucl. Mater.* 366 (2007) 8–27.

- [4] J.D. Higgs, B.J. Lewis, W.T. Thompson, Z. He, A conceptual model for the fuel oxidation of defective fuel, *J. Nucl. Mater.* 366 (2007) 99–128.
- [5] W.T. Thompson, B.J. Lewis, E.C. Corcoran, M.H. Kaye, S.J. White, F. Akbari, Z. He, R. Verrall, J.D. Higgs, D.M. Thompson, T.M. Besmann, S.C. Vogel, Thermodynamic treatment of uranium dioxide based nuclear fuel, *Int. J. Mater. Res.* 98 (2007) 1004–1011.
- [6] B.J. Corse, FORM 2.0 – Fuel Oxidation and Release Model – A Computer Code to Predict the Low Volatile Fission-Product Release and Fuel Volatilization from Uranium Dioxide Fuel Under Severe Reactor Accident Conditions (M.Sc Thesis), Royal Military College of Canada, Kingston, ON, 1997.
- [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 (Ph.D Dissertation), Queen's University, Kingston, ON, 2001.
- [8] J.D. Higgs, Modelling Oxidation Behaviour in Operating Defective Nuclear Reactor Fuel Elements (Ph.D Dissertation), Royal Military College of Canada, Kingston, ON, 2006.
- [9] S.J. White, Phase Equilibria in Nuclear Fuel Containing Dysprosium (M.Sc Thesis), Royal Military College of Canada, Kingston, ON, 2006.
- [10] K. Shaheen, A Semi-Empirical Oxidation Model for Defective Nuclear Fuel (M.Sc Thesis), Royal Military College of Canada, Kingston, ON, 2007.
- [11] M.J. Welland, Simulation of Melting Uranium Dioxide Nuclear Fuel (Ph.D Dissertation), Royal Military College of Canada, Kingston, ON, 2009.
- [12] E.C. Corcoran, Thermochemical Modelling of Advanced CANDU Reactor Fuel (Ph.D Dissertation), Royal Military College of Canada, Kingston, ON, 2009.
- [13] M.H.A. Piro, Computation of Thermodynamic Equilibria Pertinent to Nuclear Materials in Multi-Physics Codes (Ph.D Dissertation), Royal Military College of Canada, Kingston, ON, 2011.
- [14] K. Shaheen, A Mechanistic Code for Intact and Defective Nuclear Fuel Element Performance (Ph.D Dissertation), Royal Military College of Canada, Kingston, ON, 2011.
- [15] M.H. Kaye, W.T. Thompson, B.J. Lewis, F.C. Iglesias, Oxidation of nuclear fuel rods during a loss-of-coolant accident, in: Proceedings of the 8th Canadian Material Science Conference, London, ON, June 12, 1996.
- [16] M.H. Kaye, W.T. Thompson, B.J. Lewis, Toward a comprehensive thermodynamic treatment of noble metal inclusions, *Trans. Am. Nucl. Soc.* (1998) 123–125.
- [17] J.D. Higgs, B.J. Lewis, W.T. Thompson, Z. He, Proceedings of the 9th International Conference on CANDU Fuel, Belleville, ON, 2005.
- [18] F. Akbari, M.J. Welland, B.J. Lewis, W.T. Thompson, Proceedings of the 9th International Conference on CANDU Fuel, Belleville, ON, 2005.
- [19] B.J. Lewis, W.T. Thompson, J.D. Higgs, F. Akbari, M.H. Kaye, C. Thurgood, J. Serdula, C. Morrison, COG Report – COG-04-2043, Toronto, ON, 2005.
- [20] W.T. Thompson, B.J. Lewis, M.H. Piro, E.C. Corcoran, M.H. Kaye, J.D. Higgs, F. Akbari, D.M. Thompson, RMC Fuel Thermochemical Treatment, an online appendix to B.J. Lewis, W.T. Thompson and F.C. Iglesias In: R.J.M. Konings (Ed.), Fission Product Chemistry in Oxide Fuels, Comprehensive Nuclear Materials, Elsevier, 2012.
- [21] C.W. Bale, A.D. Pelton, W.T. Thompson, Facility for the Analysis of Chemical Thermodynamics – User Manual 2.1, Ecole Polytechnique de Montreal/McGill University, Canada, 1996.
- [22] C.W. Bale, P. Chartrand, S.A. Degterov, G. Eriksson, K. Hack, R. Ben Mahfoud, J. Melançon, A.D. Pelton, S. Petersen, FactSage thermochemical software and databases, *CALPHAD* 26 (2) (2002) 189–228.
- [23] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, 2nd ed., Pergamon Press plc, Oxford, England, 1997.
- [24] Y. Miyake, H. Matsuzaki, T. Fujiwara, T. Saito, T. Yamagata, M. Honda, Y. Muramatsu, Isotopic ratio of radioactive iodine ($^{129}\text{I}/^{131}\text{I}$) released from Fukushima Daiichi NPP accident, *Geochim. J.* 46 (2012) 327–333.
- [25] WHO/SDE/PHI/99.6 (English only), Guidelines for Iodine Prophylaxis following Nuclear Accidents – Update 1999, World Health Organization, Geneva, (1999). (http://www.who.int/ionizing_radiation/pub_meet/Iodine_Prophylaxis_guide.pdf).
- [26] S.G. Prussin, D.R. Olander, W.K. Lau, L. Hansson, Release of fission products (Xe, I, Te, Cs, Mo, and Tc) from polycrystalline UO_2 , *J. Nucl. Mater.* 154 (1988) 25–37.
- [27] H. Kleykamp, The chemical state of the fission products in oxide fuels, *J. Nucl. Mater.* 131 (1985) 221–246.
- [28] H. Kleykamp, J.O.A. Paschoal, R. Pejasa, F. Thümmel, Composition and structure of fission product precipitates in irradiated oxide fuels: correlation with phase studies in the Mo-Ru-Rh-Pd and BaO- UO_2 - ZrO_2 - MoO_3 systems, *J. Nucl. Mater.* 130 (1985) 426–433.
- [29] H. Kleykamp, The chemical state of the fission products in oxide fuels within the different stages of the nuclear fuel cycle, in: P. Vincenzini (Ed.), High Tech Ceramics, Elsevier Science Publishers, Amsterdam, Netherlands, 1987, pp. 2769–2798.
- [30] H. Kleykamp, The chemical state of fission products in oxide fuels at different stages of the nuclear fuel cycle, *Nucl. Technol.* 80 (1988) 412–422.
- [31] P.G. Lucuta, R.A. Verrall, H. Matzke, B.J. Palmer, Microstructural features of SIMFUEL – simulated high-burn-up UO_2 -based nuclear fuel, *J. Nucl. Mater.* 178 (1991) 48–60.
- [32] Physical Design – Design of Reactor Facilities: Nuclear Power Plants, Regulatory Document REGDOC-2.5.2, Canadian Nuclear Safety Commission, Ottawa, ON, May 2014.
- [33] Safety Analysis – Deterministic Safety Analysis, Regulatory Document REGDOC-2.4.1, Canadian Nuclear Safety Commission, Ottawa, ON, May 2014.
- [34] Safety Analysis – Probabilistic Safety Assessment (PSA) for Nuclear Power Plants, Regulatory Document REGDOC-2.4.2, Canadian Nuclear Safety Commission, Ottawa, ON, May 2014.
- [35] D.R. Olander, Fundamental Aspects of Nuclear Reactor Fuel Elements, Technical Information Center, Virginia, 1976.
- [36] D. Cubicciotti, A model for release of fission gases and volatile fission products from irradiated UO_2 in steam environment, *Nucl. Technol.* 53 (1981) 5–7.
- [37] D. Cubicciotti, Vaporization thermodynamics of fission products from fuel under nuclear-accident conditions, *Adv. Ceram.* 17 (1986) 211–222.
- [38] D. Cubicciotti, B.R. Sehgal, Vapour transport of fission products in postulated severe light water reactor accidents, *Nucl. Technol.* 65 (5) (1984) 266–291.
- [39] D. Cubicciotti, Vapour transport of fission products under nuclear-accident conditions, *J. Nucl. Mater.* 154 (1988) 53–61.
- [40] S. Yamanaka, K. Kurosaki, Thermophysical properties of Mo-Ru-Rh-Pd alloys, *J. Alloy. Compd.* 353 (2003) 269–273.
- [41] S. Imoto, Chemical state of fission products in irradiated UO_2 , *J. Nucl. Mater.* 140 (1986) 19–27.
- [42] Private Conversation with Dr. R. McEachern at COG Meeting of October 28, 1996.
- [43] E.C. Corcoran, B.J. Lewis, W.T. Thompson, J. Mouris, Z. He, Controlled oxidation experiments of simulated irradiated UO_2 fuel in relation to thermochemical modelling, *J. Nucl. Mater.* 414 (2) (2011) 73–82.
- [44] H. Kleykamp, The solubility of selected fission products in UO_2 and $(\text{U,Pu})\text{O}_2$, *J. Nucl. Mater.* 206 (1993) 82–86.
- [45] W.L. Lyon, W.E. Baily, The solid-liquid phase diagram for the UO_2 - PuO_2 system, *J. Nucl. Mater.* 22 (3) (1967) 332–339.
- [46] I. Yu., Belyaev, Radiokhimiya 25 (6) (1983) 791–794.
- [47] T.D. Chikalla, C.E. McNeilly, J.L. Bates, J.J. Rasmussen, International Colloquium on the Study of Crystalline Transformation at High Temperature Above 2000 K, Odeillo, France, 1971.
- [48] S. Dash, D.D. Sood, R. Prasad, Phase diagram and thermodynamic calculations of alkali and alkali earth metal zirconates, *J. Nucl. Mater.* 228 (1) (1996) 83–116.
- [49] F.T. Ewart, R.G. Taylor, J.M. Horspool, G. James, The chemical effects of composition changes in irradiated oxide fuel materials II-fission product segregation and chemical equilibria, *J. Nucl. Mater.* 61 (1976) 254–270.
- [50] T. Itaki, K. Kono, H. Tachi, S. Yamonouchi, S. Yuhara, I. Shibahara, Irradiation performance of experimental fast reactor “JOYO” MK-I driver fuel assemblies, *J. At. Energy Soc. Jpn.* 27 (1985) 435–449.
- [51] K. Kurosaki, M. Uno, Phase equilibria in the ternary URu_3 - URh_3 - UPd_3 system, *J. Alloy. Compd.* 271–273 (1998) 641–644.
- [52] L.C. Wang, M.H. Kaye, Thermodynamic evaluation of the U-Ru-Rh-Pd quaternary system with emphasis on the UPd_3 - URh_3 - URu_3 metallic system, UNENE R&D Workshop, Toronto, ON, December, 2011.
- [53] L.C. Wang, M.H. Kaye, A re-examination of thermodynamic modelling of U-Ru phase diagram, in: Proceedings of the 39th Annual CNS/CNA Student Conference, Saint John, NB, 2015.
- [54] L.C. Wang, The Other Metallic Inclusion In Burned Up Nuclear Fuel A Thermodynamic Evaluation of the U-Ru-Rh-Pd Quaternary System (Ph.D Dissertation), University of Ontario Institute of Technology, Oshawa, ON, (in preparation).
- [55] P.G. Lucuta, R.A. Verrall, H. Matzke, B.J. Palmer, Microstructural features of SIMFUEL – simulated high-burnup UO_2 -based nuclear fuel, *J. Nucl. Mater.* 178 (1) (1991) 48–60.
- [56] V. Kuznetsov, Mo-O-U (Molybdenum-Oxygen-Uranium), in: G. Effenberg, S. Ilyenko (Eds.), Non-Ferrous Metal Systems. Part 4, Springer, Berlin Heidelberg, Germany, 2007, pp. 328–336.
- [57] R.A. Barry, J. Deveau, I. Korobkov, E.C. Corcoran, J. Scott, A facile and accurate preparation of pure UMoO_6 and a crystallographic study of a Na-U-Mo-O intermediate, *Polyhedron* 108 (2016) 143–150.
- [58] R.A. Barry, A. Novel, Synthesis and Thermodynamic Investigation of UMoO_6 (M.Sc Thesis), Royal Military College of Canada, Kingston, ON, 2015.
- [59] E.V. Suleimanov, A.V. Golubev, E.V. Alekseev, C.A. Geiger, W. Depmeier, V. G. Krivovichev, A calorimetric and thermodynamic investigation of uranyl molybdate UO_2MoO_4 , *J. Chem. Thermodyn.* 42 (7) (2010) 873–878.
- [60] E.F. Juenke, S.F. Bartram, Crystallographic data on UO_2WO_4 and UO_2MoO_4 , *Acta Crystallogr.* 17 (1964) 618.
- [61] A. Fedoseev, N. Budantseva, A. Yusov, M. Grigor'ev, New molybdates of hexavalent actinides, *Radiokhimiya* 5 (1990) 14–18.
- [62] M.H.A. Piro, J. Banfield, K.T. Clarno, S. Simunovic, T.M. Besmann, B.J. Lewis, W.T. Thompson, Coupled thermochemical, isotopic evolution and heat transfer simulations in highly irradiated UO_2 nuclear fuel, *J. Nucl. Mater.* 441 (2013) 240–251.
- [63] K.T. Clarno, B. Philip, W.K. Cochran, R.S. Sampath, S. Allu, P. Barai, S. Simunovic, M.A. Berrill, L.J. Ott, S. Pannala, G.A. Dilts, B. Mihaila, G. Yesilyurt, J. Ho Lee, J. E. Banfield, The AMP (Advanced MultiPhysics) nuclear fuel performance code, *Nucl. Eng. Des.* 252 (2012) 108–120.
- [64] I. Gauld, O. Hermann, R. Westfall, ORIGEN scale system module to calculate fuel depletion, actinide transmutation, fission product buildup and decay, and associated radiation terms, Technical Report, ORNL/TM-2005/39, Version 6, vol. II, Sect. F7, Oak Ridge National Laboratory, TN, 2005.
- [65] M.H.A. Piro, S. Simunovic, T.M. Besmann, B.J. Lewis, W.T. Thompson, The Thermochemistry Library Thermochemica, *Comput. Mater. Sci.* 67 (2013) 266–272.
- [66] M.H.A. Piro, T.M. Besmann, The thermochemistry library thermochemica and its applications to multi-physics simulations, in: Proceedings from the TMS 2013 142nd Annual Meeting, San Antonio, TX, 2013, pp. 371–378.

- [67] M.J. Welland, W.T. Thompson, B.J. Lewis, D. Manara, Computer simulations of non-congruent melting of hyperstoichiometric uranium dioxide, *J. Nucl. Mater.* 385 (2009) 358–363.
- [68] D. Manara, C. Ronchi, M. Sheindlin, M. Lewis, M. Brykin, Melting of stoichiometric and hyperstoichiometric uranium dioxide, *J. Nucl. Mater.* 342 (2005) 148–163.
- [69] B. Cox, Pellet-clad interaction (PCI) failures of zirconium alloy fuel cladding – a review, *J. Nucl. Mater.* 172 (3) (1990) 249–292.
- [70] G.A. Ferrier, M. Farahani, J. Metzler, P.K. Chan, E.C. Corcoran, Mitigating the stress corrosion cracking of zircaloy-4 fuel sheathing – siloxane coatings revisited, *J. Nucl. Eng. Radiat. Sci.* 2 (2016).
- [71] J. Metzler, G.A. Ferrier, E.C. Corcoran, Influence of Alkali Metal Oxides and Alkaline Earth Metal Oxides on the Mitigation of Stress Corrosion Cracking in CANDU Fuel Sheathing, in: Proceedings of the 39th Annual CNS/CNA Student Conference, Saint John, NB, 2015.
- [72] D. R. Stull, H. Prophet, JANAF Thermochemical Tables. Washington, D.C: US Department of Commerce, National Bureau of Standards/Institute for Applied Technology, 1985.
- [73] M.W. Chase, NIST-JANAF Thermochemical Tables, U.S. Department of Commerce, Washington, D.C, 1998.
- [74] I. Barin, O. Knacke, O. Kubaschewski, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, 1973, Supplement 1997.
- [75] E.H.P. Cordfunke, R.J.M. Konings, Thermochemical Data for Reactor Materials and Fission Products, Elsevier Science Publishers, Amsterdam, 1990.
- [76] L.V. Gurvich, I.V. Veyts, C.B. Alcock, Thermodynamic Properties of Individual Substances, 1989.
- [77] M.H. Kaye, W.T. Thompson, Chapter 9. computation of pourbaix diagrams at elevated temperature, in: R.W. Revie (Ed.), Uhlig's Corrosion Handbook., 3rd ed., John Wiley and Sons, New York, United States, 2011, pp. 111–122.
- [78] H.E. Barner, R.V. Scheuerman, Handbook of Thermochemical Data for Compounds and Aqueous Species, Wiley-Interscience, New York, NY, 1978.
- [79] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston, TX, 1974.
- [80] O. Palazhchenko, Pourbaix Diagrams at Elevated Temperatures: A Study of Zn and Sn (M.Sc Thesis), University of Ontario Institute of Technology, Oshawa, ON, Canada, 2012.
- [81] M.H. Piro, G.M.F. Bruni, B.J. Lewis, W.T. Thompson, F.C. Iglesias, G. Ma, R. Nashed, J.G. Roberts, Computation of actinide pourbaix diagrams at 298 K and 550 K (U, Np, Pu, Am, Cm – H₂O), in: Proceedings of the 11th International Conference on CANDU Fuel, Niagara Falls, ON, 2010.