

BENCHMARKING A FISSION-PRODUCT RELEASE COMPUTER PROGRAM CONTAINING A GIBBS ENERGY MINIMIZER

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ABSTRACT - The computer program SOURCE IST 2.0 contains a 1997 model of fission-product vaporization, developed by B.J. Corse et al. That model was tractable on computers of that day. However, the understanding of fuel thermochemistry has advanced since that time. A new prototype computer program was developed with: a) newer Royal Military College of Canada thermodynamic model of uranium dioxide fuel, b) new model for fission-product vaporization from the fuel surface, c) a user-callable thermodynamics subroutine library, d) an updated nuclear data library, and e) an updated nuclide generation and depletion algorithm. The prototype has been benchmarked against experimental results.

Nomenclature

IESO	(Ontario) Independent Electricity System Operator
IST	Industry Standard Toolset, a set of computer programs adopted by the Canadian nuclear industry for safety analysis
Nuclear species	Nuclides and nuclear isomers
RMC	The Royal Military College of Canada in Kingston, Ontario
SC11	A prototype computer program for estimating fission-product release fractions from uranium-dioxide fuel (source term) incorporating an internal chemical solver (ChemApp) and based on SOURCE IST 2.0P11
SC11E	A shorthand label for SC11 with a database that eliminates solid caesium trizirconate solid, Cs ₂ Zr ₃ O ₇ (s)
SOURCE 2.0	The Canadian Industry Standard Toolset computer program for calculating fission-product release fractions from uranium-dioxide fuel
SOURCE IST 2.0P11	A production version of SOURCE 2.0, released by OPG in 2008 January
VICTORIA	A computer program with mechanistic models of radionuclide behaviour in the reactor coolant system under severe accident conditions

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Introduction

In 2012, nuclear power stations provided 56.4% of the electricity produced in Ontario [1]. Part of the licensing of these stations is analysis of postulated accidents in which radioactive material is released to the environment. One step in that release (and its analysis) is the release of fission products from fuel. Within the Canadian nuclear industry, the Industry Standard Toolset (IST) provides computer programs for nuclear safety analysis. The IST computer program for fission-product release from fuel is SOURCE 2.0 [2, 3]. The version on which this work is based is SOURCE IST 2.0P11. All version of SOURCE IST 2.0 to date contain a 1997 model of fission-product vaporization by Corse *et al.* [4-6]. The 1997 model was tractable on desktop computers of that date.

In the intervening years, both computing power and the understanding have fuel thermochemistry have improved. A newer thermodynamic model of irradiated uranium dioxide fuel has been developed by RMC researchers [7-10]. Additionally, the interactive thermodynamics package FACT [11, 12], used in the 1997 work, has evolved into FactSage [13, 14]. The core solvers of FactSage are available in the commercial thermodynamics subroutine library ChemApp [13]. A prototype computer program based on the 2008 January production version (SOURCE IST 2.0P11) has been created [15, 16] that incorporates: 1) the newer RMC thermochemical treatment of irradiated uranium-dioxide fuel, 2) a new model for fission-product vaporization from the fuel surface, 3) the user-callable ChemApp thermodynamics subroutine library, 4) a revised list of nuclides and nuclear isomers in the fuel and updated and corrected nuclear physics data, and 5) minor updates to the nuclide generation and depletion algorithm.

Recently-published work [15, 16] identified improved agreement between calculated and experimental release fractions for ^{140}La , in particular, as an advantage of the new prototype computer program. The same works recommended repeating the benchmarking of release fractions with caesium trizirconate solid, $\text{Cs}_2\text{Zr}_3\text{O}_7$ (s), removed from the thermochemical database. This solid was observed in the calculated equilibrium composition of one test case in which the calculated caesium release fraction was lower than the experimental release fraction. The purpose of this paper is to report the prototype development more widely, and to report the results of that benchmarking exercise.

1 Background

1.1 SOURCE 2.0

Descriptions of the phenomena modelling in the computer program SOURCE 2.0 were presented at a previous CANDU Fuel Conference [3]. Only a brief summary will be provided here. For normal operating conditions, SOURCE 2.0 models thermal fission of ^{235}U , ^{239}Pu and ^{241}Pu and fast fission of ^{238}U and the accumulation of radiologically-significant fission-product nuclides and nuclear isomers from these fissions. Diffusion of fission products within fuel grains to the grain-boundary is modelled using a numerical solution to a one-dimensional Booth diffusion model [17, 18] on an unevenly spaced mesh. Diffusion is coupled to fission-product generation from fission, branching decay [19-21] and neutron-induced transformations and depletion from decay transformation [22, 23]. The mesh is finer near the surface of the grains. The perfect-sink boundary has been retained for all chemical elements, for the time being. After grain growth, a shell of fuel oxide with no fission products is added to the outside the grain. The fission-product concentration on the

mesh of the new grain is recalculated by interpolation, retaining the zero-gradient Neumann boundary condition at the centre of the grain and the zero concentration Dirichlet boundary condition at the mesh location corresponding to the old grain radius. Grain-boundary sweeping reduces the grain concentration by the fraction of the grains swept and adds this material to the grain surface. Grain-boundary bubbles grow to interconnection and on interconnection vent excess gas. These models are similar to those in FREEDOM [24]. The gas in the gap is vented at fuel failure.

Simple rules are applied to phase changes that form liquid phases (fuel/Zircaloy interaction, fuel dissolution by molten Zircaloy, and fuel melting) based on the user-input fraction of the fuel in liquid form at the end of each time interval. Congruent releases are assumed due to matrix stripping and fuel leaching using input phase fractions. Thermodynamic equilibria were calculated [4-6] for varying oxygen potential, fission-product to gas ratios, pressure and temperature using the inventory of a CANDU fuel element at a burnup of $100 \text{ MW}\cdot\text{h}\cdot\text{kgU}^{-1}$ to produce lookup tables. The Corse model of fission-product vaporization from fuel surfaces used these lookup tables and a diffusion-limited mass-transfer model to compute release rates. After fuel failure, gas from the coolant (inert gas, hydrogen steam and oxygen) is allowed to enter the fuel-to-sheath gap. The gas composition is used in selecting the appropriate lookup table. The Corse model, in its day, represented an advancement of the state-of-the-art for fission-product release modelling.

1.2 The SC11 prototype

The SC11 prototype replaced the Corse model [4]. The new model calculates a new equilibrium composition among the material in the gap (including a user-defined fraction of the gas flowing by the fuel), solid or liquid inclusions on the fuel surface, and the actinides and oxygen from the fuel matrix. Fission products within the grains do not participate in the reaction because they are held up by slow diffusion or in intragranular bubbles. Material in the grain-boundary bubbles does not participate in the equilibrium because the bubbles are not in direct contact to the fuel surface. The ChemApp solver is used to calculate chemical equilibrium at the end of each time interval using the current inventories. The nuclide generation and depletion model was modified to accommodate a larger number of nuclear species, longer decay and transformation chains, and a larger degree of branching. Other models within SOURCE IST 2.0P11 were left unchanged deliberately.

2 Computer program configuration

SC11E consists of three components: the program executable, the thermochemical database and the physics database. The databases are text files that should not be altered by users. For this exercise, the executable and the physics database were unaltered from the work previously reported [15, 16]. The thermochemical database is the RMC thermodynamic model of irradiated uranium dioxide fuel used previously [8-10], with the exception of the deletion of the solid compound caesium trizirconate ($\text{Cs}_2\text{Zr}_3\text{O}_7(\text{s})$). The other aspect of configuration of the test cases is the configuration of the input files for the test cases. These were based on the 18 SOURCE 2.0 validation cases distributed on behalf of OPG on the CD-ROM for the release of the production version, SOURCE IST 2.0P11, 2008 January. The validation cases were set up so that the same input files were used for all comparisons. Two cases have been revised from those on the distribution CD-ROM.

2.1 Discussion of caesium trizirconate

In previous work [15, 16], the presence of solid caesium trizirconate, $\text{Cs}_2\text{Zr}_3\text{O}_7(\text{s})$, resulted in lower releases of ^{134}Cs and ^{137}Cs than experimentally observed in one test case. Two papers [25, 26] reported the existence of caesium trizirconate synthesized in impure form from CsNO_3 and ZrO_2 at 1000 C. These two papers contained no thermodynamic data for the compound. The thermodynamic data in the RMC model are referenced to the computer program VICTORIA and to unpublished work at Sandia National Laboratory [27, 28]. No experimental thermodynamic data have been located for $\text{Cs}_2\text{Zr}_3\text{O}_7(\text{s})$.

In work by Mishra [29], synthesis of Cs_2ZrO_3 by the sol-gel process from nitrate solution with ignition at 400 C with excess citric acid and annealing at 600 C lead to the presence of ZrO_2 in their product which was attributed to vaporization of $\text{Cs}_2\text{O}(\text{g})$ and $\text{CsOH}(\text{g})$ during ignition. Under these conditions, there was no evidence in the X-ray diffraction pattern of the rich X-ray diffraction pattern reported by Plyushchev and Grizik [25, 26]. Based on the lack of reliable thermodynamic data and of clear evidence for the existence of this compound, it was deleted from the database for this work.

3 Benchmarking of nuclide release fractions

In the following figures, the SOURCE IST 2.0P11 results are plotted in solid symbols and labelled P11 in the legend. The earlier SC11 results are plotted with open squares (labelled SC11), and the latest results are plotted as crosses (labelled SC11E). The diagonal line represents ideal agreement between the calculated release fraction and the experimental release fraction. Only four figures are presented: ^{134}Cs and ^{137}Cs to demonstrate the improvement achieved in this latest work, ^{140}La to demonstrate that the results are the same as for SC11, and ^{85}Kr to demonstrate that modelling fission-product chemistry has no impact on noble gas releases, which are the same for the test cases using in all three computer programs configurations (P11, SC11 and SC11E).

3.1 Benchmarking ^{134}Cs and ^{137}Cs

The results for ^{134}Cs and for ^{137}Cs are plotted in Figure 1 and Figure 2, respectively. The new results for SC11E reproduce the older SC11 results except in one case. This is the lowest temperature air case (maximum temperature 1313 K). In previous work [15, 16], the reduced releases compared to P11 were reported to be due to the existence of $\text{Cs}_2\text{Zr}_3\text{O}_7(\text{s})$ in the calculated equilibrium composition. The new release fraction (from SC11E) is higher than that from SC11, but lower than that from SOURCE IST 2.0P11 (labelled P11)).

In the SOURCE IST 2.0P11 results there is no caesium remaining on the fuel surface. In the SC11 results, the condensed phase on the fuel surface is $\text{Cs}_2\text{Zr}_3\text{O}_7(\text{s})$, caesium trizirconate. In the SC11E results, the predicted condensed phase on the fuel surface is $\text{Cs}_2\text{U}_7\text{O}_{22}(\text{s})$, caesium heptauranate. The molar quantity of caesium in the condensed phase is smaller in the SC11E case than in the SC11 case. The remaining caesium is accounted for by increased releases of caesium from the fuel. This result are consistent with the hypothesis that caesium trizirconate should not exist under these conditions. However, it could also be argued that the thermodynamic data for caesium trizirconate are inaccurate and that it should exist but in smaller quantities than originally calculated from the data used in the SC11 calculation.

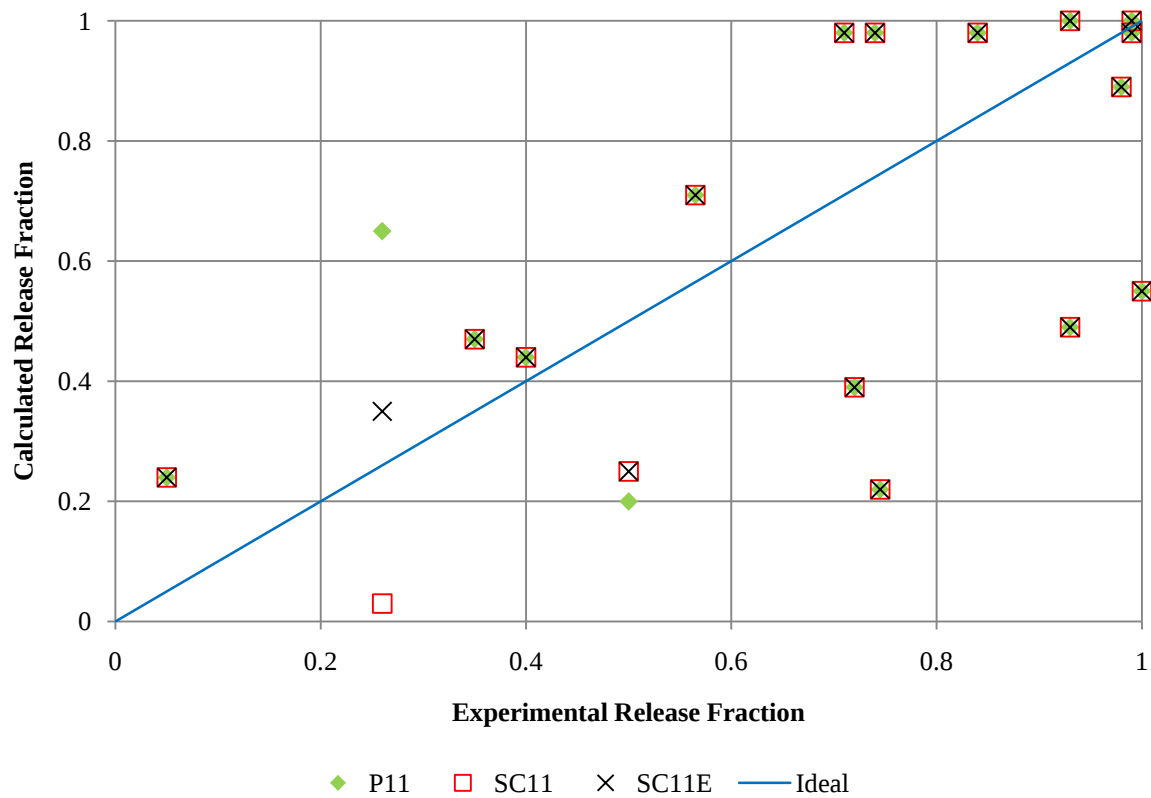


Figure 1: Comparison of Calculated and Experimental Release Fractions of ^{134}Cs

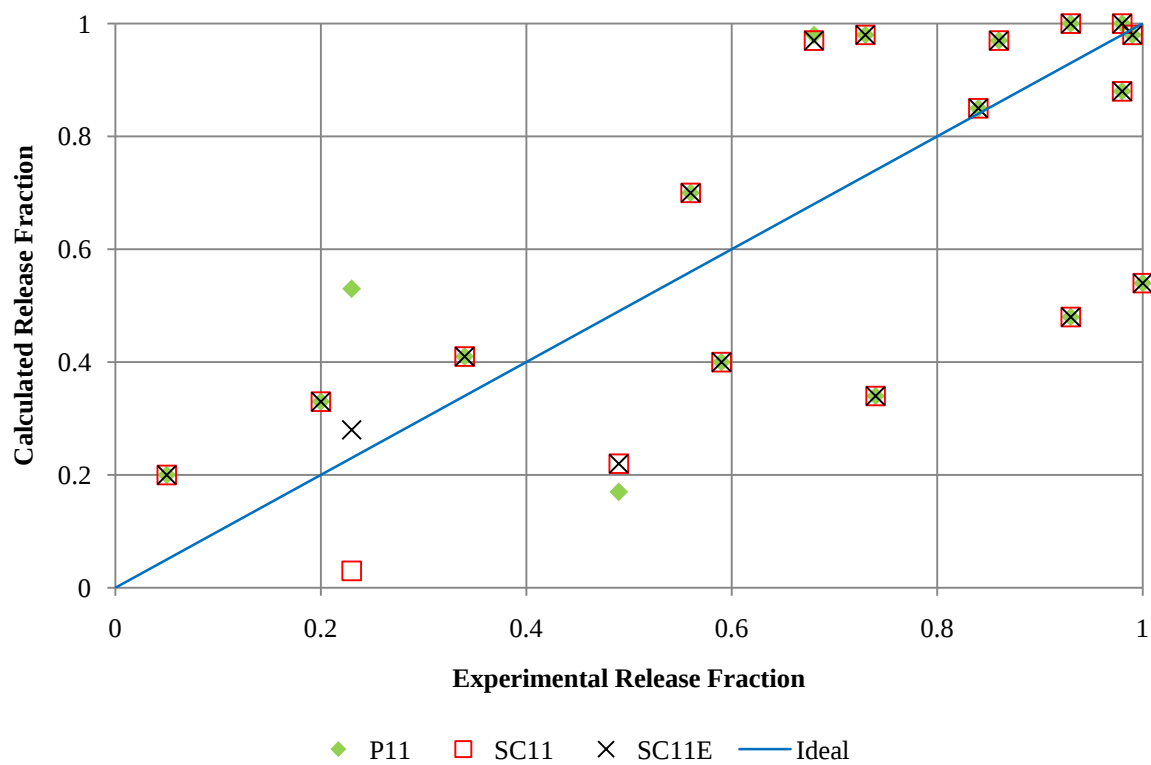


Figure 2: Comparison of Calculated and Experimental Release Fractions of ^{137}Cs

3.2 Benchmarking ^{140}La

It is prudent to demonstrate that the previously-observed improvement in ^{140}La release fractions is also demonstrated by these newer results. With the large degree of interaction among actinide and fission-product elements, it is possible that a change in one compound could have an impact indirectly on another, apparently unrelated, chemical element. The release fractions for ^{140}La are plotted in Figure 3. As can be seen the results labelled SC11E match those labelled SC11 and are unaltered by the deletion of caesium trizirconate from the thermochemical database. The change from SOURCE IST 2.0P11 was attributed [15, 16] to the model of the uranium dioxide fluorite phase with dissolved fission products [8]. Because lanthanum oxide is soluble in uranium dioxide, the calculated equilibrium composition has a much lower total vapour pressure of lanthanum-containing species than earlier thermodynamic calculations. The results are also closer to experiments measurements than code results that do not consider fuel thermochemistry.

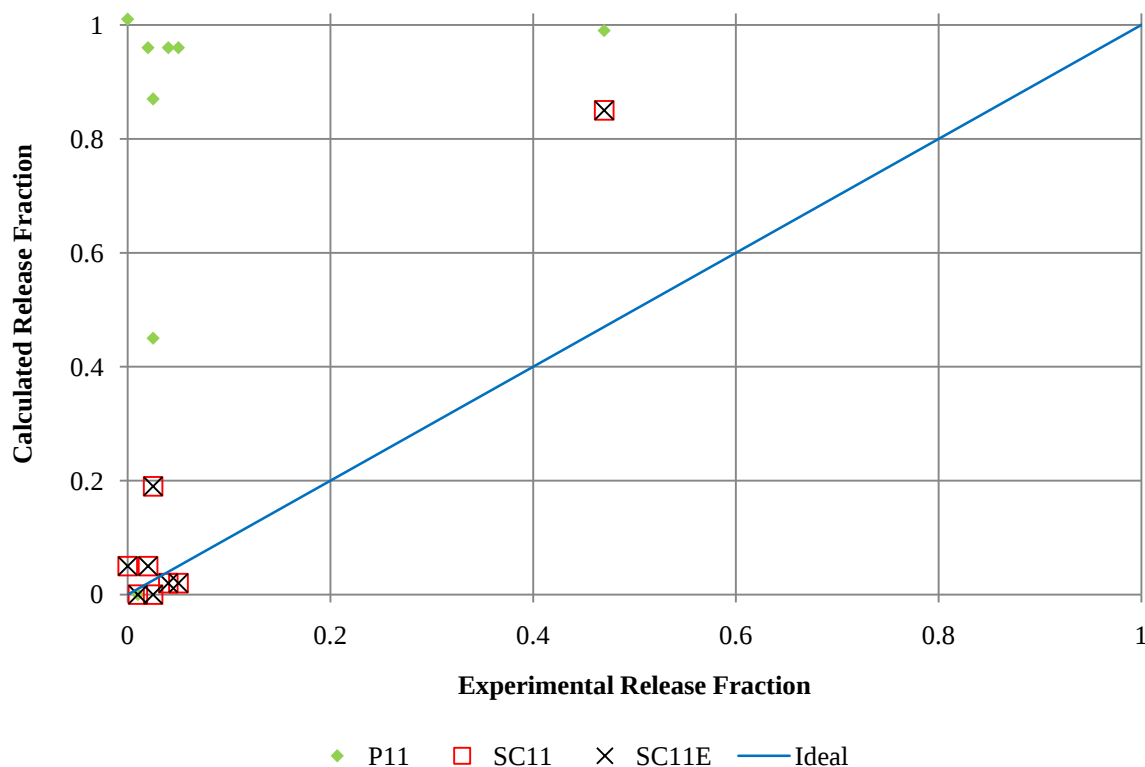


Figure 3: Comparison of Calculated and Experimental Release Fractions of ^{140}La

3.3 Benchmarking ^{85}Kr

The calculated release fractions for ^{85}Kr are unaltered by deleting caesium trizirconate from the thermochemical database (see Figure 4). Krypton is represented in the RMC model [7-10] as an equivalent molar quantity of xenon. Xenon (like krypton) is an inert gas and does not interact with chemical elements in the fuel. Thus, it is expected that changes to the chemical database would not affect the release fractions for ^{85}Kr .

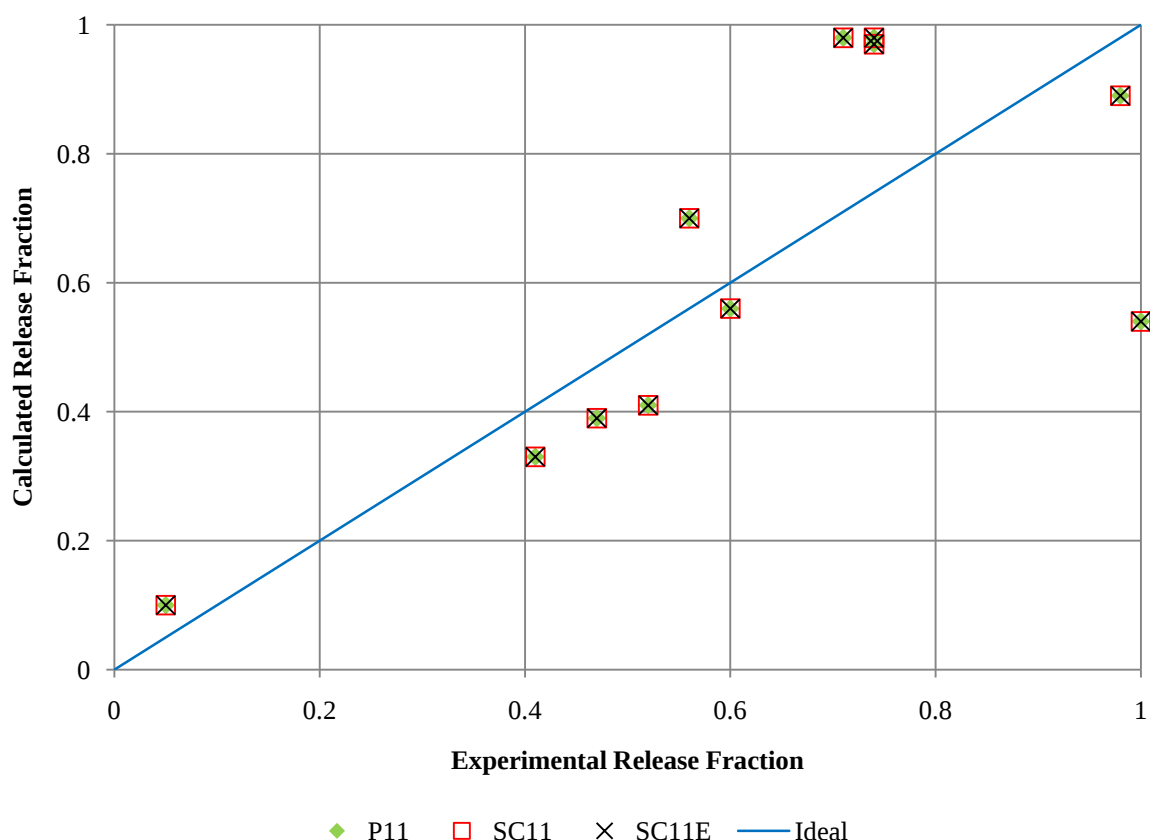


Figure 4: Comparison of Calculated and Experimental Release Fractions of ^{85}Kr

3.4 Other nuclides

Final release fractions of ^{95}Zr , ^{95}Nb , ^{103}Ru , ^{106}Ru , ^{125}Sb , ^{131}I , ^{133}Xe , ^{135}Xe , ^{140}Ba , ^{144}Ce , ^{144}Pr and ^{154}Eu were also unaffected by the deletion of caesium trizirconate from the thermochemical database. Data for these nuclides were previously published [15].

3.5 Benchmarking summary

The removal of caesium trizirconate from the database has improved the agreement between calculated and experimental release fractions for one case. In this low-temperature air test (maximum temperature 1313 K, 1040°C), the improvement in the release fractions of ^{134}Cs and ^{137}Cs is the direct result of the removal of a compound that would have stabilized more caesium in the condensed phase. Releases of ^{137}Cs show a similar change. Final release fractions of ^{85}Kr , ^{95}Zr , ^{95}Nb , ^{103}Ru , ^{106}Ru , ^{125}Sb , ^{131}I , ^{133}Xe , ^{135}Xe , ^{140}Ba , ^{140}La , ^{144}Ce , ^{144}Pr and ^{154}Eu were also unaffected by the deletion of caesium trizirconate from the thermochemical database.

4 Implications

The implications of this work confirm the conclusions of earlier work [15, 16]. It is now tractable to include a Gibbs energy minimize into a computer program for calculating fission-product release fractions. The presence of lanthanum oxide as in solution with uranium

dioxide is an important mechanism for improving the accuracy of predictions of lanthanum release from fuel.

While removing caesium trizirconate from the thermodynamic database for irradiated uranium-dioxide fuel has resulted improved agreement with the experimental release fractions, the thermodynamics of the caesium oxide (Cs_2O)/zirconium oxide (ZrO_2) remains ill-defined.

5 Conclusions

The general conclusions of previous work remain valid.

1. It is tractable to include an internal Gibbs energy minimizer in a computer program to calculate fission-product release fractions.
2. The model of the fluorite phase (uranium dioxide plus fission products, usually as oxides) contributes to improved accuracy of lanthanide release fractions.

Conclusions of this specific exercise can be drawn.

3. Only one test case was affected by the deletion of $\text{Cs}_2\text{Zr}_3\text{O}_7$ (s) from the thermochemical database for this work: a test reaching 1313 K in air (the lowest temperature test in air).
4. The removal of caesium trizirconate results in increased releases of caesium when a solid compound that keeps caesium in the condensed phase is deleted. This is the desired effect. At the relatively low temperature of this test, some caesium is predicted to remain in a solid phase on the fuel surface in the form of caesium heptauranate, $\text{Cs}_2\text{U}_7\text{O}_{22}$ (s).
5. No deleterious side-effects of deleting caesium trizirconate were observed in this exercise.

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7 References

- [1] Independent Electricity System Operator, "Ontario's Independent Electricity System Operator Releases 2012 Electricity Production, Consumption and Price Data", IESO News Release 2013 January 11, http://www.ieso.ca/imoweb/media/md_newsitem.asp?newsID=6323, last retrieved 2013 February 23.

- [2] A.C. Brito, F.C. Iglesias, Y. Liu, M.A. Petrilli, M.J. Richards, R.A. Gibb and P.J. Reid, "SOURCE 2.0: A Computer Program to Calculate Fission Product release from Multiple Fuel Elements for Accident Scenarios", Proceedings of the 4th International Conference on CANDU Fuel, Pembroke, 1995 October 1-4, Vol.2, pp. 5B-45-5B-56.
- [3] D.H. Barber, F.C. Iglesias, L.W. Dickson, M.J. Richards and P.J. Reid, "SOURCE IST 2.0: Phenomena Modelling", Proceedings of the 7th International Conference on CANDU Fuel, Kingston, 2001 September 23-27, Vol. 2, pp. 5C-21-5C-30
- [4] 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 Accident Conditions", M. Eng. Thesis, Royal Military College of Canada, Kingston, Ontario, 1997
- [5] B.J. Lewis, B.J. Corse, W.T. Thompson, M.H. Kaye, F.C. Iglesias, P. Elder, R.S. Dickson and Z. Liu, "Vaporization of Low-Volatile Fission Products Under Severe CANDU Reactor Accident Conditions", Proceedings of the 5th International Conference on CANDU Fuel, Toronto, 1997 September 21-27, Vol.1, pp. 145-159.
- [6] B.J. Lewis, B.J. Corse, W.T. Thompson, M.H. Kaye, F.C. Iglesias, P. Elder, R. Dickson and Z. Liu, "Low Volatile Fission-Product Release and Fuel Volatilization During Severe Reactor Accident Conditions", *Journal of Nuclear Materials*, Vol.252, No.3, 1998, pp. 235-256.
- [7] B.J. Lewis and W.T. Thompson, "Fuel Engineering Chemistry Research at the Royal Military College of Canada", Proceedings of the 9th International Conference on CANDU Fuel, Belleville, 2005 September 18-21
- [8] 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 and S.C. Vogel, "Thermodynamic Treatment of Uranium Dioxide Based Nuclear Fuel", *International Journal of Materials Research*, Vol.98, No.10, 2007, pp 1004-1011
- [9] E.C. Corcoran, "Thermochemical Modelling of Advanced CANDU Reactor Fuel", Ph.D. Thesis, Royal Military College of Canada, Kingston, Ontario, 2009
- [10] M.H.A. Piro, "Computation of Thermodynamic Equilibria Pertinent to Nuclear Materials in Multi-Physics Codes", Ph.D. Thesis, Royal Military College of Canada, 2011
- [11] W.T. Thompson, C.W. Bale and A.D. Pelton, "Teaching Chemical Thermodynamics Applications with the FACT Interactive Computing System", *Engineering Education*, 1979, pp. 201-205.
- [12] W.T. Thompson, C.W. Bale and A.D. Pelton, "Interactive Computer Tabulations of Thermodynamic Properties with the F*A*C*T System", *Journal of Metals*, Vol.32, No.12, 1980, pp. 18-22.

- [13] G. Eriksson and E. Königsberger, "FactSage and ChemApp: Two Tools for the Prediction of Multiphase Chemical Equilibria in Solutions", *Pure and Applied Chemistry*, Vol.80, No.6, 2008, pp. 1293-1302.
- [14] C.W. Bale, A.D. Pelton, W.T. Thompson, G. Eriksson, K. Hack, P. Chartrand, S. Dectorov, I-H. Jung, J. Melançon and S. Petersen, "FactSage 6.3", *Computer Database and Software, Thermfact and GTT-Technologies*, 2012.
- [15] D.H. Barber, "Implementation of a Thermodynamic Solver within a Computer Program for Calculating Fission-Product Release Fractions", *Ph.D. Thesis, Royal Military College of Canada*, 2013.
- [16] D.H. Barber, "Implementation of a Gibbs Energy Minimizer in a Fission-Product Release Computer Program", *AECL Nuclear Review*, Vol.2, No.1, 2013, pp. 39-48.
- [17] A.H. Booth, "Method for Calculating Fission Gas Diffusion from UO₂ Fuel and Its Application to the X-2-f Loop Test", *AECL Report AECL-496*, 1957
- [18] A.H. Booth, "A Suggested Method for Calculating the Diffusion of Radioactive Rare Gas Fission Products from UO₂ Fuel Elements and a Discussion of Proposed In-Reactor Experiments that May Be Used to Test Its Validity," *AECL-700, Atomic Energy of Canada Limited*, 1957
- [19] E. Rutherford, "Radio-activity", 2nd Edition, *Cambridge University Press*, Cambridge, Great Britain, 1905
- [20] H. Bateman, "The Solution of a System of Differential Equations Occurring in the Theory of Radio-active Transformations", *Proceedings of the Cambridge Philosophical Society*, Vol.15, 1910, pp. 423-427.
- [21] G.F. Thomas and D.H. Barber, "Stiffness in Radioactive Decay Chains", *Annals of Nuclear Energy*, Vol.21, No.3, 1994, pp. 309-320.
- [22] P.J. Reid, B.J. Lewis, F.C. Iglesias and D.H. Barber, "Modelling of Intra-Granular Diffusion, Production and Removal in SOURCE 2.0", Proceedings of the 6th International Conference on CANDU Fuel, Niagara Falls, Ontario, Canada, September 26-30, 1999, Vol. 2, pp. 249-257.
- [23] G.V. Kidson, "A Generalized Analysis of the Cumulative Diffusional Release of Fission Product Gases from an "Equivalent Sphere" of UO₂", *Journal of Nuclear Materials*, Vol.88, No.2-3, 1980, pp. 299-308
- [24] L.D. Macdonald, D.B. Duncan, B.J. Lewis and F.C. Iglesias, "FREEDOM: A Transient Fission Product Release Model for Radioactive and Stable Species", Presented at the International Atomic Energy Agency Technical Committee Meeting on Water Reactor Fuel Element Computer Modelling in Steady-State, Transient and Accident Conditions, Preston, England, September 18-22, 1988, pp. 203-208 (also available as Report AECL-9810, 1989 May).

- [25] V.E. Plyushchev and A.A. Grizik, “Alkali Metal Zirconates and Hafnates”, Redkie Shchelochnye Elementy; Sbornik Dokladov Vsesoyunogo Soveshchaniya po Redkim Shchelochnym Elementam, 2nd (1964), Novosibirsk, Soviet Union, pp. 201-218, (In Russian).
- [26] A.A. Grizik and V.E. Plyushchev, “Existence of Caesium Zirconates and Hafnates”, Izvestiya Vysshikh Uchebnykh Zavedenii, Tsvetnaya Metallurgiya, Vol.11, No.5, 1968, pp. 53-59, (In Russian).
- [27] T.J. Heames, D.A. Williams, N.E. Bixler, A.J. Grimley, C.J. Wheatley, N.A. Johns M.D. Vine, P. Domagala, L.W. Dickson, C.A. Alexander, I. Osborn-Lee, S. Zawadzki, J. Rest, and H.S. Bond, “VICTORIA: A Mechanistic Model of Radionuclide Behavior in the Reactor Coolant System Under Severe Accident Conditions”, Rev. 1, SAND90-0756, NUREG/CR-5545, Sandia National Laboratories, 1992
- [28] N.E. Bixler, “VICTORIA 2.0: A Mechanistic Model for Radionuclide Behaviour in a Nuclear Reactor Coolant System Under Severe Accident Conditions”, Sandia National Laboratories, NUREG/CR-6131, SAND93-2301 R3, 1998
- [29] R. Mishra, M. Ali, S.R. Bharadwaj and D. Das, “Preparation of Cs_2ZrO_3 and Cs_2ThO_3 through Sol-Gel Method and Their Characterization”, Journal of Thermal Analysis and Calorimetry, Vol.66, No.3, 2001, pp. 779-784.