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Section 1. Nuclear fuel and ceramics

Review of the materials-chemistry models in the VICTORIA code [1]

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Abstract

Recently a Peer Review Committee established by the US Nuclear Regulatory Commission issued its report on VICTORIA, a detailed mechanistic computer code that addresses the release of fission products from degraded reactor fuel and the ex-core behavior of the released material. The present paper summarizes the findings of the report relevant to the materials-chemistry aspects of the code that apply chiefly to the high-temperature, steam–hydrogen environment of the degrading fuel and cladding. In addition to reviewing the theoretical foundation of the mechanisms used in the code, the assessment utilizes the 'test problem' technique. In this method, the code (or its methods) are applied to very simple fuel and cladding systems with variations of input conditions, code flags, and material properties. The output is judged against expected behavior for each change. The topics treated include the thermochemical database, the code's method of treating interphase equilibria, the model of fission product release, and the treatment of cladding oxidation and hydrogen production. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Models of severe accident phenomena in nuclear reactors have long been utilized by plant designers, operators, and the regulators as an essential adjunct to the safe design and operation of nuclear power plants. After the accident at Three Mile Island Unit 2, the US Nuclear Regulatory Commission (NRC) embarked on a severe accident research program. The goals of this program were to gain a better understanding of the challenges to the plant during accident progression and the effectiveness of various mitigation systems and strategies, and, in particular, to reassess the technical bases for predicting the possible source terms due to severe accidents [1]. A suite of computer codes collectively called the 'Source Term Code Package' emerged in the mid-1980s from this effort [2]. Due partly to the complexity of the phenomena involved, the development of NRC-sponsored codes intended to model plant behavior under severe accident conditions has evolved into a two-tier strategy. The first tier consists of detailed mechanistic codes focused on key specific aspects of severe accidents and the second tier consists of system level codes used to perform integrated analyses [3].

VICTORIA is a detailed mechanistic code intended to model radionuclide release from degraded fuel and the transport of the released products during the in-vessel stage of accident progression at light water reactors. The code requires as input an initial inventory of radionuclides present in the fuel and the time- and position-dependence of the fluid's temperature, pressure, velocity, mass and momentum in the core during the event. The code then calculates the transport of fission products from the interior to the surface of the degraded fuel and then to the coolant channel through breaks in the cladding. The fission products are allowed to react chemically under the assumption that instantaneous thermodynamic equilibrium is achieved among the reactants which form an ideal solution. The partial pressures of the species overlying the fuel compared to the

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species equilibrium partial pressures establish a driving force for release or condensation. VICTORIA contains detailed models of aerosol transport and deposition through various geometries within the primary coolant system. The code also calculates the decay heating of surfaces within the primary system from deposited radionuclides and the subsequent revaporization or resuspension of the deposited material.

The NRC appointed a committee in 1995 to conduct an independent, peer review of version 1.0 of the VICTORIA code as documented in the code manual [4]. The objectives of the review were to provide an assessment of the modeling capability embodied in the code and the adequacy of its documentation. The review was conducted along the guidelines established in earlier reviews of other NRC-sponsored severe accident codes, in particular, the reviews of the MELCOR code [5], the CONTAIN code [6] and the SCDAP/RELAP5 code [7]. These guidelines provided for both a 'bottoms-up' review of the individual models contained in the code as well as a 'top-down' review of the code against a set of targeted applications and design objectives provided to the committee by the NRC.

This paper is based on the results pertaining to materials chemistry issues contained in the report issued by the VICTORIA Peer Review Committee [8]. Section 2 of the paper provides an overview of the thermochemical database and an evaluation of its adequacy for performing chemical equilibria calculations in the temperature range pertaining to severe accidents. It also includes an assessment of the rare earth fission products covered in the code and the method for calculating the equilibrium pressures of the rare earth oxides. The code's treatment of nonstoichiometric urania in computing oxygen pressures under both oxidizing and reducing conditions is evaluated. Interphase chemical equilibrium and the assumption in the code of a single ideal solution of all species present at a solid or liquid surface exposed to a gas phase is reviewed in Section 3. The fission product release model(s) embedded in the code are analyzed in Section 4. The VICTORIA code does not perform thermal-hydraulic calculations but accepts, as input, data from systems level codes such as MELCOR or SCDAP/RELAP5. However, VICTORIA includes a module for evaluating the kinetics of Zircaloy oxidation by steam. This module is based, as in other NRC-sponsored accident codes, on the parabolic scaling model. Section 5 evaluates the limitations of this model and compares its predictions with a model based on integral diffusion theory.

The latest version of the code was utilized to make a series of runs on a simple test problem consisting of a stack of bare fuel pellets inside an inert cylindrical container exposed to a flowing gas. In most runs, the gas was pure hydrogen. In a few cases, mixtures of steam and hydrogen were used. The test problem was used to determine the sensitivity of the code to the choices of key parameters and to compare the code predictions against independent calculations of selected models. Insights from the test problem impacting the materials chemistry models in VICTORIA are referred to in various places in Sections 2–5 below, and in more detail in Ref. [8].

2. Equilibrium chemistry

The thermochemical database of the VICTORIA code includes 26 elements and 288 molecular species for which temperature-dependent Gibbs free energies of formation are provided. The majority of the entries are for fission product compounds, including oxides, hydroxides, and compounds involving two fission products. The compounds of PWR control rod elements (Cd, Ag, In) and boron supplied by the coolant are also represented. Significantly, no carbon compounds are included in the database, which limits the applicability of the code to pressurized light water reactors, at least for materials chemistry in the core. Application of the code to accidents in boiling water reactors (BWRs) is problematic because of the boron carbide material in BWR control blades. The elements of stainless steel and the compounds of zirconium and tin in LWR cladding and structures are included.

Three aspects of the VICTORIA thermochemical database are worth detailed inspection: (i) its accuracy; (ii) its completeness; and (iii) the validity of the method used to extrapolate Gibbs free energies of formation to the very high temperatures (>2000 K) expected in severe core-damage accidents.

The thermochemical information in VICTORIA is an eclectic mixture obtained from various literature sources. It consists of a third-order (cubic) polynomial expression for the Gibbs free energy, G, of each molecular species as a function of temperature, T:

$$G(T) = A + BT + CT^2 + DT^3. \quad (1)$$

A review of an earlier version of the 167-species database contained in the 1990 release of the VICTORIA code was performed by Ball et al. [9]. This review consisted of comparing both the G–T data used and the calculated G values in the VICTORIA database with G values from other standard databases and sources, in particular, Refs. [10–15], over selected temperature ranges. In cases where the source of the data used in VICTORIA and the other database were the same, the comparison served as a check on the extent of agreement of Eq. (1) with the values in the other database. Ball et al. [9] review is not a comparison of VICTORIA's database with experimental data. Rather, the comparison is with other databases, some of which (e.g., Ref. [13]) were also used in assembling VICTORIA's database.

Of the data for 167 species that were assessed, G values in the VICTORIA database for 17 species were found to differ by more than 10% from the values in the assessed databases. For another 10 species, the difference was between 5% and 10%. Sources of the differences were ascribed in some cases to extrapolation of the data to cover the range from 500 to 3000 K and in other cases to the use of a polynomial to fit the available data.

After Ball et al. review of the original VICTORIA database was completed, another 121 species have been added to the 1992 version [4]. No systematic assessment of the thermochemical data pertaining to these additional species has been performed. However, a critique of the data on 16 compounds was carried out by Thompson and Kaye [16]. This assessment demonstrated that Eq. (1) can lead to extrapolation errors at higher temperatures. They show that for 13 out of the 16 species assessed, in the 2000–3000 K temperature range, the heat capacity calculated with the coefficients A–D in Eq. (1) becomes negative, an impossible physical property. Thompson and Kaye point out that in place of the cubic polynomial fit of Eq. (1), the following theoretically based formulation is preferred

$$G(T) = a + bT - cT \ln T, \tag{2}$$

where a, b, and c are fitting constants for each species. They demonstrate that refitting the $G(T)$ data with the Eq. (2) produces physically reasonable specific heats for the 16 species assessed.

2.1. Fission products

The second deficiency identified by Thompson and Kaye [17] deals with the accuracy of the Gibbs free energies of the hydroxides of Eu, the only rare earth in the database. Reliable data for $M(OH)$, $M(OH)_2$, and $M(OH)_3$ are given by Cubiocciotti [18] for $M = La$, Ce, Pr, and Nd. In addition, Thompson and Kaye [17] show that the VICTORIA code's values for the corresponding Eu hydroxides do not fit in with the trends observed for the other lanthanide hydroxides.

A potentially serious omission of the VICTORIA thermochemical database is the restriction of the rare earths to the low-yield element Eu. Fission products not accounted for include Ce, Pr, Gd, La, Nd, Dy, and Y. Ignoring these species can skew the equilibrium chemistry calculations since the rare earths consume oxygen even if they remain in the fuel as trivalent cations. The absence of gadolinium is particularly worrisome, since this element (in its nonradioactive form) is added to most fuel as a burnable poison. Of the noble metal fission products, only ruthenium is treated. Tc, Rh, and Pd are missing from the database. On a mass basis, only two thirds of the fission products are accounted for in VICTORIA. With the lanthanides restricted to Eu, only 1% of the rare earths are included in the thermochemistry.

The missing rare earths and noble metals are generally of lower volatility and radiological importance as compared, for example, with elements such as iodine, cesium, and tellurium. However, most of the codes used to perform consequence calculations of radiological releases include several of these rare earths and noble metals in their dosimetry routines. The MACCS consequence code [19], for example, includes isotopes of Ce, Y, La, Pr, Nd, Tc, and Rh.

The VICTORIA code's method of calculating equilibrium pressures of fission product oxides contains a fundamental flaw, which can be illustrated by the rare-earth element, M. Since the thermochemical database contains the free energy of formation of the sesquioxide, the vaporization equilibrium is described in the code by the reaction

$$\tfrac{1}{2}M_2O_3(\text{sol'n}) = MO(g) + \tfrac{1}{4}O_2 \tag{3a}$$

and the corresponding mass-action law

$$\frac{p_{MO}p_{O_2}^{1/4}}{z_M^{1/2}} = \exp\left(-\frac{\Delta G^0}{RT}\right), \tag{4}$$

where z_M is the cation fraction of M^{3+} in the oxide lattice and

$$\Delta G^0 = \tfrac{1}{4}G(O_2) + G(MO(g)) - \tfrac{1}{2}G(M_2O_3(s)) \tag{5}$$

is obtained from the thermochemical database. However, the correct vaporization reaction is [20]

$$MO_{3/2}(\text{sol'n}) = MO(g) + \tfrac{1}{4}O_2, \tag{3b}$$

which has the ΔG^0 given by Eq. (5) but a mass action law in which the exponent of z_M in Eq. (4)) is unity instead of 1/2. This implementation error in VICTORIA produces significant overprediction of fission product oxide pressures when the concentrations in the solid solution are low.

In addition to classical gas–solid thermochemistry, the current version of the VICTORIA code provides an option permitting application of bulk equilibrium chemistry to species residing within the grains of the fuel. From a physical point of view, however, the thermochemical database is not applicable to the fission product species present inside the lattice of UO_2. In the fuel, the fission products exist as atoms. It is unrealistic, for example, to postulate the presence of a CsI molecule inside the fluorite structure of UO_2, or that its stability can be predicted by bulk thermodynamic properties. The energy required to form such a molecule in the lattice is enormous. Grimes and Catlow [21] have calculated the stable forms of many fission products in the lattice of uranium dioxide; in no instance is a molecular species the stable form. This option is to be eliminated in the next version of the code, but at least one other code similar to VICTORIA [22] has adopted this erroneous notion.

2.2. Urania

Of all the molecular species considered in VICTORIA, $UO_3(g)$ is accorded conflicting treatment. The equilibrium pressure of this species can be calculated from the general thermochemical database of the code, or from a separate equation presented in the code manual [4]. The two methods give results that differ by at least an order of magnitude. Assessment of UO_3 pressures from various sources is given in a separate contribution to this issue [23].

The oxygen pressure in the gas phase is important because it controls the stable species of volatilized fission products (e.g., Eq. (3b)) as well as the volatility of the fuel as $UO_3(g)$. VICTORIA calculates the oxygen pressure as a part of its gas–phase equilibrium analysis. An oxygen potential model is a correlation that relates the O_2 partial pressure with the O/U ratio of the fuel and the temperature. Conventional models [24,25] represent the solid as hypo-or hyperstoichiometric urania, which are fluorite structures with an oxygen deficiency or an oxygen excess.

VICTORIA, on the other hand, simulates non-stoichiometric urania by changing the relative proportions of the pseudo components $U, UO_2, U_4O_9, \ldots$ in the hypothetical ideal solid solution chosen to represent the fuel. The relative amounts of these species respond to the ambient O_2 pressure according to the equilibrium of reactions such as

$$U(sol'n) + O_2(g) = UO_2(sol'n) \tag{6}$$

in a reducing environment, and

$$8UO_2(sol'n) + O_2(g) = 2U_4O_9(sol'n) \tag{7}$$

in an oxidizing environment. The O/U ratio of the fuel is then determined by the appropriate ratio of O-containing and U-containing species in the solid.

Different solution models can be used for interpreting $p_{O_2}(x, T)$ data for $UO_{2\pm x}$. Blackburn [24] represents UO_{2+x} as a pseudo-binary solution of stoichiometric UO_2 and neutral atomic oxygen. Lindemer and Besmann [25] employ several hypothetical U_aO_b species in their representation of urania. VICTORIA's error is not in the choice of solution species but in applying bulk thermochemistry to them; that is, in applying the standard free energies from the database to compute the equilibrium constants for the reactions in Eqs. (6) and (7).

Table 1
Urania stoichiometry from VICTORIA and Blackburn's models for $p_{O_2} = 6 \times 10^{-14}$ (atm)

	O/U Ratio	
Temperature (K)	VICTORIA	Blackburn
2200	2.000	2.000
2400	1.931	1.957
2500	1.526	1.865
2600	0.606	1.681

Tables 1 and 2 compare the VICTORIA $p_{O_2}(x, T)$ predictions and those of the Blackburn model. In Table 1, the oxygen pressure is fixed at a value sufficiently low that the urania is hypostoichiometric and Eq. (6) is activated in the VICTORIA method. In Table 2, the O_2 pressures are calculated for specified T and O/U ratios greater than two. In both examples, significant deviations between the two methods are observed. Replacement of the current oxygen potential methodology in VICTORIA is clearly needed.

3. Interphase chemical equilibria

In VICTORIA, vapor-solid equilibrium is invoked between the bulk coolant gas and (i) bounding structures (e.g., cladding, core internals, piping) and (ii) aerosol particles suspended in the flow. Interphase equilibrium is also established between the gas in the pores in the fuel and the surface of the pore. The bulk coolant does not interact directly with the fuel because cladding is always assumed to be present. This restriction caused considerable difficulties for the code in a simple test problem involving bare fuel exposed to a steam-hydrogen gas mixture [8]. Consequently, the ability of the code to deal properly with the chemical interaction between gas and core debris is problematic.

Two aspects of the method of handling gas–solid equilibria in VICTORIA warrant consideration. The first is the use of hypothetical 'films' or 'layers' in the

Table 2
Stoichiometry – oxygen pressure relationships in UO_{2+x}

	Oxygen pressure (atm)		
Temperature (K)	O/U ratio	VICTORIA	Blackburn
2500	2.0140	5.0×10^{-7}	3.6×10^{-5}
2500	2.0014	4.0×10^{-9}	3.5×10^{-7}
2600	2.0158	1.0×10^{-6}	7.6×10^{-5}
2600	2.0018	1.0×10^{-8}	1.0×10^{-6}

adjacent phases invoked by VICTORIA in order to perform interphase chemical equilibrium calculations. The second is the assumption of a homogeneous, ideal condensed phase adjacent to the gas.

3.1. Fictitious films

VICTORIA uses hypothetical 'chemistry films' on solid surfaces and in the adjacent gas for the purpose of providing volumes of material for performing equilibrium calculations. On solid surfaces, the chemistry film is taken to be 5 nm thick. In fuel pores, all species are assumed to mix completely with the uranium oxides in the 'chemistry film'.

The second type of 'film' is in the gas phase adjacent to the solid chemistry film. The thickness of the chemistry film in the gas is taken to be an arbitrary fraction of the estimated gas-phase mass transfer boundary layer. The species in this gas-phase film are assumed to be in chemical equilibrium with species in the solid (or liquid) film.

The solid/liquid and gaseous films used as modeling constructs have no physical basis and are introduced solely to permit the equilibrium chemistry module to function. They may compromise the chemistry calculations in VICTORIA. The test problem (a bare stack of fuel pellets in flowing H_2 for 500 s) was run with the code for different values of these fictitious film thicknesses [8]. The results are shown in Table 3. As modeling constructs designed to facilitate the equilibrium calculations, the values of the film thicknesses should have no effect on the output. However, at 2673 K, both solid and gaseous film thicknesses affect the computed fractional releases by factors as large as four. At 1873 K, only the solid film thickness has an effect.

There is no reason why fictitious films are needed to perform interphase equilibrium calculations. Basically, VICTORIA deals with a complex variant of transport in two adjacent phases at whose common interface chemical equilibrium prevails. This situation has been treated in the chemical engineering literature for seven decades.

3.2. Condensed phases at solid surfaces

The solid or liquid exposed to a gas phase is assumed to be a single ideal solution of pure species in the thermochemical database, including urania. A single phase is assumed irrespective of possible phase-diagram constraints on mutual solubility.

The single-condensed-phase treatment used in VICTORIA can lead to inaccuracies even when the solution is ideal. For example, the code determines cesium volatility by vaporization from the 'chemistry film' at the solid surface

$$\mathrm{CsI(sol'n)} = \mathrm{CsI(g)}. \tag{8}$$

If CsI is dissolved in the fuel along with other fission products, its activity is much less than unity and hence its partial pressure is much less than the vapor pressure. However, CsI is not soluble in either oxidic or metallic condensed phases, and if it condensed, it would probably do so as a separate (third) phase. Such an assignment would significantly increase the CsI pressure over that from a single condensed phase in which CsI is diluted by other species, including the fuel. While accurate prediction of the condensed phases present in a mixture of fission products and fuel is not possible, assignment of all species to a single phase is neither correct nor conservative. The revised version of the code will permit three phases: an oxide, a metal phase, and a third phase consisting of fission product iodides. This phase assemblage is present only on fuel surfaces exposed to a gas.

4. Fission product release

The foundation of VICTORIA's fission product release model is a combination of series and parallel process originating in the fuel grains and terminating at the bulk coolant. The sequence of steps is shown in Fig. 1.

Table 3
Effect of chemistry film thicknesses on fractional releases – test problem

	Chemistry film		Fractional release				
Temperature (K)	On fuel (nm)	In gas [a]	Ba	Sr	Te	Eu	Xe
2673	5	0.1	0.20	0.18	0.72	0.05	1.00
2673	50	0.1	0.05	0.05	0.28	0.02	1.00
2673	5	0.05	0.14	0.10	0.61	0.02	1.00
1873	5	0.1	10^{-5}	0	0.016	0	0.09
1873	50	0.1	10^{-5}	0	0.003	0	0.11
1873	5	0.05	10^{-5}	0	0.016	0	0.09

[a] Expressed as a fraction of the gas-phase boundary layer thickness.

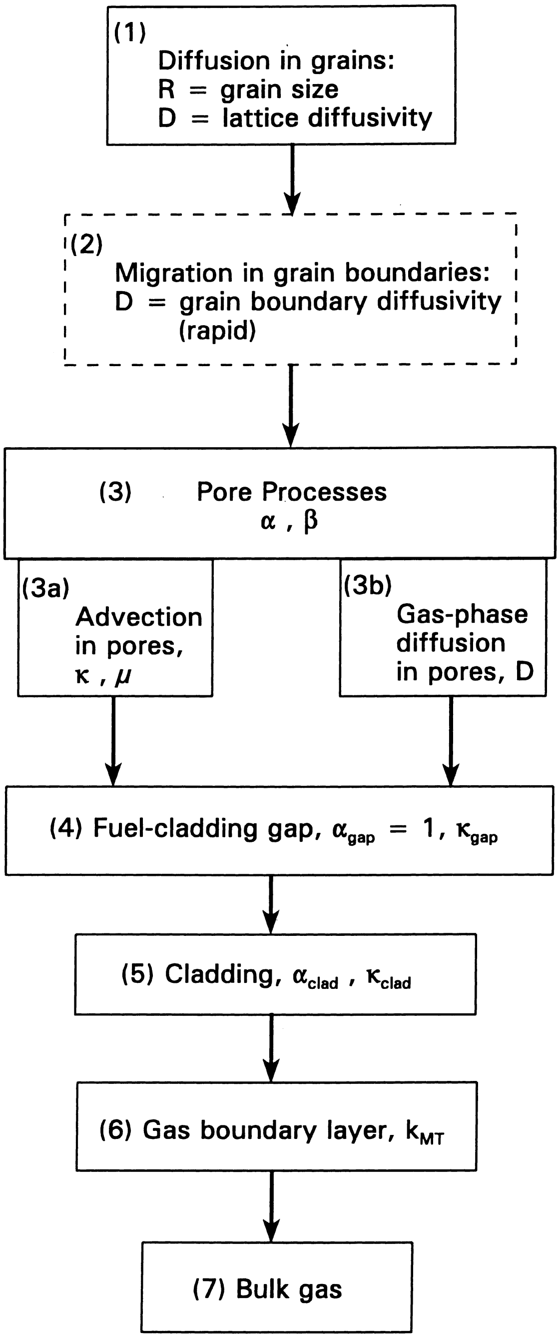

Fig. 1. Fission-product transport processes in fuel element as modeled by VICTORIA.

4.1. Release from the grains

Fission-product transport from the grain interior to the grain boundary is represented by a simple Booth diffusion process. The diameter of the Booth sphere is assumed to be that of the as-fabricated fuel grain. Grain growth during normal operation or during the accident transient is neglected on the grounds that the grain boundaries are locked in place by fission gas bubbles or precipitates. In VICTORIA, fractional releases are expressed by the asymptotic formulas

$$\begin{aligned} f &= \tfrac{6}{\sqrt{\pi}}\sqrt{\tau} - 3\tau \quad \text{for} \quad 0 \leqslant \tau \leqslant 0.15, \\ f &= 1 - \tfrac{6}{\pi^2}\mathrm{e}^{-\pi^2\tau} \quad \text{for} \quad \tau > 0.15, \end{aligned} \tag{9}$$

where $\tau = Dt/a^2$, with a is the grain radius and D the current value of the diffusion coefficient. Severe accident scenarios invariably involve time-dependent fuel temperatures, which causes fission product diffusion coefficients to be time-dependent. No account is taken of this effect in the code, although this oversimplification can be rectified by use of a "compressed time" in Fick's law

$$t^* = \frac{1}{D(t)}\int_0^t D(t')\,\mathrm{d}t'. \tag{10}$$

Because D is a continuously increasing function of t (at least in the first stages of an accident), the appropriate time t^* for use in Eq. (9) is shorter than the clock time. Failure to account for this effect results in overprediction of the release fractions.

The original Booth release model was conceived for fission gases, for which the boundary condition for the diffusion equation at the surface of the grain is zero concentration. In VICTORIA this condition had to be relaxed; otherwise there would be no coupling between the intragranular diffusion process and the subsequent steps in Fig. 1. The code deals with fission products of low volatility by allowing for non-zero concentrations of these species at the grain surface. The grain surface concentrations are those in the 'chemistry film' at the pore surface where interphase equilibrium with the gas in the porosity is assumed. The effect of any time dependence of the grain-surface concentration of fission products on the mathematical solution of the in-grain diffusion problem is not contained in Eq. (9).

By ignoring solubility limitations and mixing all fission products and fuel in a single ideal solid solution in the 'chemistry film', VICTORIA fails to account for solubility effects on release. For example, two species with similar volatilities of their pure oxide (or elemental) forms but different solubilities in UO_2 will have significantly different release rates, with the fuel-insoluble species escaping more readily than the soluble species [26]. Ignoring the possibility of second-phase formation at the pore surface underestimates the release rate of fission products with low solubilities in UO_2. Of particular significance is CsI, which is immiscible in UO_2. The vapor pressure of undiluted CsI at the pore surface is larger than that calculated by VICTORIA, where this species is diluted in UO_2 in the 'chemistry film'. The neglect of mutual solubility limitations is to be addressed in the next version of VICTORIA by permitting coexistence of three phases (Section 3.2). In addition, however, restricted solubilities of the oxides of Ba and Mo in the fuel oxide need to be considered.

VICTORIA users have generally followed the developers' practice of employing the same temperature-dependent diffusion coefficient for all fission products. The code contains a module that allows increase of the diffusivity as the fuel oxidizes, but runs with the test problem [8] indicate that this aspect is not operational. The code also exhibits other peculiar responses related to the intragranular diffusion process. Upon increasing the grain diameter in the test problem, the fractional release of several fission products increases at high temperature (2673 K), but decreases at low temperature (1873 K). Only the latter response is physically acceptable.

4.2. Grain boundary transport

Although not explicitly stated, transport from the grain boundaries to the surfaces of the internal porosity (step 2 in Fig. 1) is considered to be very rapid. VICTORIA assumes direct communication between the grain surfaces and the pore surfaces, even though these two are connected by grain boundaries.

4.3. Pore processes in the fuel

VICTORIA has pioneered the notion of pore transport as a potential rate-limiting step in fission product release. This is a bold move inasmuch as there is no experimental demonstration of this process in UO_2 fuel pellets. In the code, transport of fission products in the gas in the pores is assumed to occur by a combination of molecular diffusion and advection (Darcy flow). As indicated in step 3 of Fig. 1, these are parallel processes that are contained in the conservation equation:

$$\varepsilon_{\mathrm{tot}}\frac{\partial c}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[r\varepsilon_{\mathrm{open}}\left(D_{\mathrm{g}}\frac{\partial c}{\partial r}+\frac{c}{\varepsilon^{0}_{\mathrm{open}}}\frac{\kappa}{\mu}\frac{\partial p}{\partial r}\right)\right], \tag{11}$$

where c is the concentration of fission product in gas in pores at fuel radius r and time t, p the total gas pressure in pore at radius r, D_{g} the diffusivity of fission product in gas in pores, $\varepsilon_{\mathrm{tot}}$ the total porosity, $\varepsilon^{0}_{\mathrm{open}}$ the open porosity (superscript 0 indicates initial value), κ the permeability of solid, μ the viscosity of gas.

In principle, the diffusion term in Eq. (11) should be divided by the tortuosity to account for the deviation of the actual diffusion path from the gross radial direction.

To implement the porous-medium analysis, reliable values are needed for pellet permeability and the fraction of interconnected porosity. The total porosity is known at least for the as-fabricated fuel, but both $\varepsilon_{\mathrm{tot}}$ and $\varepsilon_{\mathrm{open}}$ increase significantly in high-burnup fuel due to the accumulation of intra- and inter-granular fission gas during normal pre-accident operation and during the accident transient. However, the value of κ recommended in the code manual can at best be described as approximate; it is at least between the values typical of sand (10^{-10} m^2) and the tuff at Yucca Mountain (10^{-18} m^2). No literature sources are given for the recommended values. The porous medium model in the VICTORIA code is perhaps appropriate to high-burnup fuel, but it does not apply to low-burnup fuel, which has not developed the network of interlinked porosity that results from fission gas bubble formation on grain faces and grain edges.

The porous medium model also causes the code's predictions to be highly sensitive to total pressure, which can vary by a factor of 150 for various accident scenarios in PWRs. Gas-phase diffusion coefficients vary inversely with the total pressure, and thus strongly influence the first term in parentheses in Eq. (11). In addition, the mass transfer coefficient at the cladding surface (step 6 in Fig. 1) depends approximately on, $D_{\mathrm{g}}^{2/3}$and so is also pressure-sensitive. No experiments demonstrating a pressure dependence of fission product release from irradiated fuel are known to exist.

In code runs with the test problem, variation of the fuel permeability by two orders of magnitude produced no change in the computed fractional releases of Ba, Sr, Te or Xe. This suggests that the advection term in Eq. (11) is small compared to the molecular diffusion term. Similarly, changing the open porosity by an order of magnitude produced no change in the computed fractional releases. At low temperature (1873 K), this insensitivity can be ascribed to release-rate limitation by intragranular diffusion. At high temperature (2673 K), however, pore diffusion should be the controlling process and the open porosity should have affected release fractions. Finally, the total porosities of 0.01 and 0.05 were used in runs with the test problem. At low temperature, no effect was observed. At high temperature, the release fractions were found to decrease with decreasing $\varepsilon_{\mathrm{tot}}$. This result is opposite of that expected; as the storage capacity of the closed porosity decreases, fission product release should increase, not decrease. The reason that commercial LWR fuel is fabricated with ~5% porosity is precisely to provide void space for fission gas collection during normal operation.

4.4. Ex-fuel processes

Fission products are delivered from the pores to the fuel-cladding gap. This zone has unit porosity, but is assigned a permeability equal to that of the cladding. Transport of fission products through the cladding is assumed to occur by the same pore-transport mechanisms as are active in the fuel. The rationale for this unconventional characterization of the cladding is that it may have ruptured, melted, or oxidized in the course of the accident.

The final step in delivering fission product to the bulk coolant is mass transfer through the gas-phase boundary layer adjacent to the cladding. The mass transfer coefficient is obtained from a conventional correlation of the Sherwood number as a function of the Reynolds and Schmidt numbers.

5. Zircaloy oxidation and hydrogen production

VICTORIA is not a full-fledged severe accident code in the sense of MELCOR, SCDAP/RELAP5, or MAAP4 because it does not perform thermal-hydraulic calculations. Instead, the code requires input of the time- and position-dependent temperatures (and flow rates) in core and in associated structures. To predict the temperatures and hydrogen production rates, the thermal-hydraulic driver code relies on a module for the kinetics of Zircaloy oxidation by steam. However, VICTORIA is armed with its own Zircaloy oxidation model from which it extracts the extent of cladding oxidation and the hydrogen produced. No attempt is made to verify that these predictions are consistent with those contained in the thermal-hydraulic driver code but not utilized by VICTORIA.

Inasmuch as the chemistry of the system is very sensitive to the oxygen potential of the bulk gas, and the latter is dictated by the H_2O/H_2 ratio, it is obviously important that H_2 production by cladding oxidation be accurately represented. For this purpose, VICTORIA utilizes the classical parabolic scaling model with the rate constant of Urbanic and Heidrick [27]. Although the conditions for the validity of the parabolic model (e.g., infinite medium, constant temperature, unlimited steam) are not satisfied in severe accidents, the parabolic model is deemed to be sufficiently accurate for use in this case although Ott [28] cautions against extrapolating it outside of its experimental domain of validity (1050–1580°C). However, parabolic scaling theory clearly breaks down under 'steam-starved' conditions, which occur when the rate of oxidation by the parabolic scaling law

$$\dot{w}_{\mathrm{corr}} = \frac{2k_T^2}{w} \tag{12}$$

is greater than the maximum rate of steam transport from the bulk gas to the surface through the hydrogen in the mass-transfer boundary layer,

$$\dot{w}_{\mathrm{MT}} = k_{\mathrm{g}} C_{\mathrm{g}} y. \tag{13}$$

In these equations, $\dot{w}$ is the rate of oxygen absorbed by the cladding per unit area, k_T is the parabolic rate constant, k_{g} is the gas-phase mass transfer coefficient, C_{g} is the total gas concentration (ideal gas law) and y is the mole fraction of steam in the bulk gas.

Even though gas-phase mass transfer forms an integral part of VICTORIA's treatment of fission product release, the code does not consider that this process can limit cladding oxidation. At each position, the code simply allows Eq. (12) to operate until the gas runs out of steam or all the Zircaloy is consumed. From this time on, the scale on the cladding is frozen in time until the remaining underlying metal melts and relocation ensues. (VICTORIA does not treat relocation; it accepts this type of information from the thermal-hydraulic driver code).

However, once steam starvation sets in and oxidation effectively ceases, two important phenomena occur, both of which are absent in VICTORIA. The first is that the oxide layer dissolves in the remaining metal. At the time of cladding melting, the previously formed oxide–metal two-phase cladding may have transformed into an all-metal cladding with a higher oxygen content than the metal had at the time of steam starvation. This phenomenon (scale dissolution) is important in the relocation process; instead of melting the remaining metal and leaving a crust of ZrO_2 on the fuel, the entire cladding melts and relocates. Relocation of bare metal cladding is easier than cladding with an oxide skin; the latter acts as a membrane and holds the molten metal in place until the skin is mechanically ruptured.

Second, zirconium is an effective getter for hydrogen, even at high temperatures. If unprotected by an oxide scale, the metal can absorb hydrogen. This has two consequences, which are described in detail elsewhere (Ref. [8] Appendix C and Ref. [29]). The dissolution of hydrogen in the metal is accompanied by release of heat that significantly adds to that produced by oxidation; the heat release augmentation due to hydrogen dissolution increases with system pressure. Unlike oxygen, hydrogen is not irreversibly taken up by the metal. Instead, H_2 is desorbed as the metal oxidizes. The result is a time lag between the production of hydrogen by metal oxidation and release from the core, a phenomenon that has been observed experimentally [30].

To reveal VICTORIA's treatment of Zircaloy oxidation, a second test problem was evaluated by the code's method (but not by the code proper) and by integral diffusion theory [31,32]. The latter methodology was developed to avoid the potential errors associated with the use of conventional parabolic kinetic rate laws, in particular their inability to account for oxide scale dissolution. In the test problem, a mixture of steam in H_2 at 1 atm total pressure flows upwards along a 15-cm length of intact cladding. The cladding tube section (1-cm OD, 1 mm wall thickness) is housed in an inert cylindrical tube with a diameter of 2 cm. The system is isothermal ($T = 1730$ K) and the flow rate ($Q = 5 \times 10^{-4}$ mol/s) and steam-hydrogen ratio of the inlet gas ($y_0 = 0.3$) are constant in time.

For computational purposes, the system is divided into three axial nodes wherein the steam mole fraction y_i

and the oxygen uptake rate, $\dot{w}_i$, are uniform but time-dependent. For the VICTORIA-method calculation, $\dot{w}_i$ is determined by the minimum of Eqs. (12) and (13) and the steam balance on cell i is given by

$$V_g C_g \dot{y}_i = Q(y_{i-1} - y_i) - A\dot{w}_i,$$

where V_g and A are the gas volume and the cladding area in the cell, respectively.

The results of the test problem calculation are best shown by a 'cladding state diagram', which displays the evolution of the cladding during the course of the simulation. This diagram shows on a time-cell number plot whether a particular cell is in one of the following states:

- under gas-phase mass control
- under solid-state diffusion control
- bare-metal cladding
- all-oxide cladding.

The last two characteristics are morphological, and are noted only when the initial oxide-metal two-phase cladding reverts completely to one of its components. The first two characteristics refer to the nature of the process currently limiting the oxygen absorption rate, independent of the morphological state.

Fig. 2 shows the cladding state diagrams for the test problem calculated by both methods. In both models, the steam entering with the carrier-gas H_2 is predicted to be completely consumed and the exit gas contains less than a few hundred parts per million of water vapor. Other features of this model comparison include:

- Gas-phase mass transfer, not solid-state diffusion, is the dominant rate-controlling process over the majority of the rod length. Had the current Zircaloy oxidation module in VICTORIA been used, all of the mass-transfer rate-limited regions in the top diagram of Fig. 2 would have been missed; VICTORIA currently does not have a mass-transfer-rate limitation option. This lack would have resulted in a considerably larger extent of cladding oxidation than shown here, with a correspondingly larger quantity of H_2 produced.
- Over the steam-starved length, the protective oxide scale disappears by dissolution in the substrate metal early in the simulation (integral diffusion method simulation only).
- The early appearance of bare metal in cell 3 is accompanied by rapid equilibrium saturation of the entire length of cladding with dissolved hydrogen that persists for the 500 s duration of the simulation.
- In the 1-atm total pressure of the test problem, hydrogen absorption augments the heat released by oxidation by only 5%. Since the quantity of hydrogen absorbed follows Sieverts' law, the heat release by hydriding of the cladding increases as the square root of the H_2 pressure.

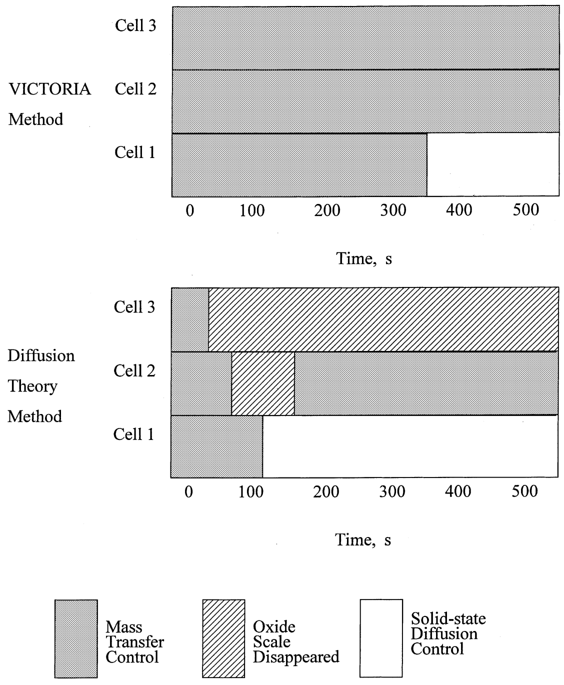

Fig. 2. Cladding state diagrams for the test problem as treated by the VICTORIA method (top) and by diffusion theory (bottom).

6. Conclusions

Chemical interactions play an important role in influencing the release and transport of fission products in severe nuclear reactor accidents. In comparison with other mechanistic codes of severe accident phenomena which treat fission product chemistry, VICTORIA includes the largest number of elements and species of those elements in its database for performing equilibrium chemical calculations in determining the source term. The review, summarized above, identifies four important materials chemistry areas where improvements are necessary to increase confidence in the code's calculational and methodological bases. The first concerns the deficiencies in the Gibbs free energy polynomial used to fit the G–T data for various species. Secondly, the treatment of nonstoichiometric urania in the code, while novel, presents problems when compared against conventional models. Third, the assumption of a single condensed phase irrespective of phase diagram constraints on mutual solubility is incorrect and needs modification. Fourth, the use of fictitious 'chemistry films' (which have no physical basis) as a purely calculational device should be eliminated as they could introduce spurious results. Code revisions are either being carried out or are planned to be undertaken in each of the above areas to rectify the identified deficiencies.

In addition, the review also highlights the treatment of Zircaloy oxidation, which is the single largest source of heat and hydrogen generation during the course of a severe reactor accident. The limitations of the parabolic kinetics model used in VICTORIA and in other systems-level codes are discussed and compared with an alternative approach based on integral diffusion theory which offers a more comprehensive understanding of the underlying phenomena.

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