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# Application of thermochemical modeling to assessment/evaluation of nuclear fuel behavior

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## ARTICLE INFO

## ABSTRACT

The combination of new fuel compositions and higher burn-ups envisioned for the future means that representing fuel properties will be much more important, and yet more complex. Behavior within the oxide fuel rods will be difficult to model owing to the high temperatures, and the large number of elements generated and their significant concentrations that are a result of fuels taken to high burn-up. This unprecedented complexity offers an enormous challenge to the thermochemical understanding of these systems and opportunities to advance solid solution models to describe these materials. This paper attempts to model and simulate that behavior using an oxide fuels thermochemical description to compute the equilibrium phase state and oxygen potential of LWR fuel under irradiation.

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## 1. Introduction

Understanding and predicting nuclear fuel behavior in power reactors has been a longstanding problem due to the complexity of phenomena and the difficulty representing them separately and in concert. For light water reactors (LWRs), which are either pressurized water (PWRs) or boiling water reactors (BWRs) and even heavy water reactors such as the CANDU systems, the fuel consists of ∼95% dense uranium dioxide pellets ∼1 cm in diameter and height, encased in a zirconium alloy cladding which then makes up a fuel rod (Table 1). Mixed oxide (MOX) fuel, i.e., fuel that consists of uranium with several percent plutonium, is also used in in some LWRs and behaves similarly. MOX used in fast neutron spectrum reactors face exacerbated fuel behavior issues due to fast neutron damage, higher average temperatures, and potentially higher burnups.

In recent years efforts to improve the oxide microstructure (form larger grains to retain noble fission product gases) or creep behavior has resulted in doping $UO_2$, for example, with $Al_2O_3$, $Cr_2O_3$, and $Nb_2O_3$ [1–3]. In addition, dopant levels of $Gd_2O_3$ are often included as burnable poisons for nuclear reactivity control early in the life of the fuel rod. While these have become common for specific fuel manufacturers or nuclear units, they will not be considered in the current analysis.

It has long been realized that the behavior of nuclear fuel depends in part on the phases present, their amounts, and their composition. In particular, oxygen potential and oxygen-to-uranium (O/U) ratio. The $UO_2$ fuel phase by itself exhibits a complicated relationship between composition (O/U ratio) and properties, exemplified by its wide homogeneity range, where it can be extensively either hypo- or hyperstoichiometric at even modestly elevated temperatures [4]. Mihaila et al. [5] and Ramirez et al. [6], for example have modeled the significant dependence of oxygen transport and thermal conductivity on the O/U ratio, and demonstrated its effect on in-reactor fuel temperature and subsequent thermal expansion/displacement. The chemical behavior also affects the adjoining cladding alloy in terms of oxidation and stress corrosion cracking caused by oxygen and corrosive fission product release from the fuel [7–9].

The ability to predict the chemical state and elemental potentials in nuclear fuel undergoing irradiation is now seen as important to accurate fuel performance modeling, whether under normal or abnormal operations. It has prompted efforts to now include thermochemical models to predict local chemical and phase states in fuel performance codes. For example, Piro et al. [10], have recently demonstrated coupling a thermochemical solver with isotopic evolution and heat transport. Efforts are underway to couple thermochemical analysis to a number of fuel performance codes.

There is substantial complexity in understanding fuel chemical behavior under irradiation that has so far prevented accurate representation. There have been, however, a number of significant efforts to understand the chemical state of fuel under irradiation ranging from direct assessment of individual elements and their

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**Table 1**
Dimensions of fuel rods for PWR and BWR systems.

| Pressurized water reactor | Boiling water reactor |
| --- | --- |
| Pellet diameter 8.19 mm | Fuel Pellet OD: 9.55 mm |
| Outside diameter 9.50 mm | Fuel Rod OD: 11.18 mm |
| Cladding thickness 0.57 mm | Clad Thickness: 0.71 mm |
| Total Rod Height: 3660 mm | Total Rod Height: 4179 mm |

likely association [11–13], experimental efforts with simulated fuels [14–19], and first principles approaches [20–22]. Thermodynamic values for fuel and fission product phases, while to various degrees still limited, have been used in several efforts to begin to treat fuel with a global thermochemical model. Imoto [17] and Cordfunke and Konings [13] examined the separate behaviors of the various fuel constituents. Corcoran et al. [23] also performed experiments with simulated fuel compositions coupled with modeling for a limited set of the important fission products. Besides Piro et al. [10] and Corcoran et al. [23] Moriyama and Furuya [24] and Loukusa et al. [25], also made some of the first efforts to apply a thermochemical free energy minimization of fuel compositions to obtain expected phase assemblages and critical values such as oxygen potential. Piro et al. [10] in particular investigated reproducing the radial oxygen potential profile across an LWR fuel pellet utilizing the computed radial burnup behavior and resulting elemental distribution. The current effort has adopted more physically representative models for the fuel and included more components within the models than have largely been previously applied. These have been used together with an evaluation of likely clad oxidation to attempt to reproduce observed burnup behavior.

## 2. Phases considered in burnup analysis

Depletion calculations were performed using ORIGEN-S [26,27] to generate transmutation and fission product compositions in typical LWR fuel with a starting O/U ratio of 2. The results are seen graphically in Fig. 1 for elements present in higher than trace amounts, with burnup to 102.5 GW d/t for a PWR 14 × 14 array fuel assembly. An example list of the elements and their concentration from significant burnup (62.5 GW d/t) is seen in Table 2. Also indicated is whether the element will likely dissolve in the fluorite structure $UO_2$ or form a secondary phase in fuel, and what type of phase following that of the review of Lewis et al. [28] and the earlier assessments noted above.

The composition and chemical activities of potential phases that will form during burnup can be computed from free energy
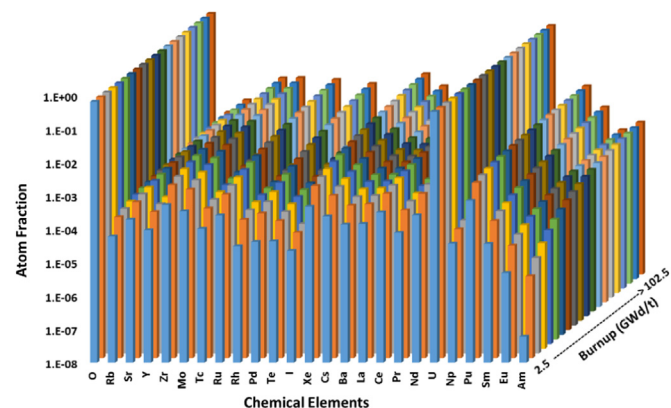


**Fig. 1.** Computed elemental fission product and transuranic atomic fractions from 2.5 to 102.5 GW d/t.

**Table 2**
Concentration of greater than trace fission product and transmutation elements generated in typical PWR fuel having undergone burnup to 62.5 GW d/t and their likely chemical form after Lewis et al. [24].

| Element | Millimole/original mol U | Secondary phase tendency | Secondary phase form |
| --- | --- | --- | --- |
| Xe | 19.25 | Strong | Elemental gas |
| Zr | 16.09 | Somewhat | Oxide |
| Mo | 15.23 | Strong | Metallic and oxide |
| Ru | 12.33 | Strong | Metallic |
| Pu | 11.88 | None | |
| Nd | 11.67 | None | |
| Cs | 9.05 | Strong | Oxide |
| Ce | 8.63 | None | |
| Pd | 7.66 | Strong | Metallic |
| Ba | 4.90 | Strong | Oxide |
| Sr | 3.93 | Strong | Oxide |
| La | 3.92 | None | |
| Pr | 3.42 | None | |
| Tc | 3.28 | Strong | Metallic |
| Sm | 2.07 | None | |
| Y | 2.05 | None | |
| Te | 1.77 | Strong | Metallic |
| Kr | 1.72 | Strong | Elemental gas |
| Rb | 1.61 | Strong | Oxide |
| Rh | 1.54 | Strong | Metallic |
| Np | 0.88 | None | Metallic |
| I | 0.80 | Strong | Elemental or iodide |
| Gd | 0.68 | None | |
| Cd | 0.67 | Strong | Metal |
| Am | 0.55 | None | |
| Eu | 0.49 | None | |
| Cm | 0.40 | None | |
| He | 0.38 | Strong | Elemental gas |
| Ag | 0.37 | Strong | Metal |
| Pm | 0.35 | None | |
| Se | 0.29 | Strong | Metallic |
| Sn | 0.27 | Strong | Metallic |
| Nb | 0.12 | Somewhat | Oxide |
| Br | 0.11 | Strong | Elemental or bromide |

minimization for the system, which are chemical equilibrium calculations. These in turn require models for variable stoichiometry phases such as the $UO_{2 \pm x}$ phase with dissolved fission products and transuranics. The resulting database for use in global equilibrium calculations for fuel undergoing burnup can be generated from the phase models and thermochemical values.

### 2.1. Fluorite structure fuel phase

The fluorite structure constituent remains the major phase in LWR fuel even at high burnup as only a small fraction of uranium is consumed [14,23,24,28,29]. The phase can accommodate substantial dissolution of +3 and +4 valence atoms, and there is an exceptionally wide composition range for the lanthanide and transuranic elements which are largely, if not exclusively, present in the phase. Zirconium, an abundant fission product is also expected to partition to a significant extent to the fluorite phase.

In the adopted approach the fluorite phase is represented by a compound energy formalism (CEF) model for $UO_{2 \pm x}$ developed by Gueneau et al. [4] after Hillert [30,31]. It is a three sublattice model with cations mixing on the first sublattice and oxygen and vacancies occupying the second (tetragonal) and third (octahedral) sublattice. Vacancies in the oxygen sublattices and the presence of a second oxygen-vacancy sublattice allow for a variable oxygen-to-metal (O/M) ratio allowing both hypo-and hyperstoichiometry. No cation vacancies or interstitials are included under the assumption that their formation are energetically unlikely.

Available system assessments for transuranic and fission