

Thermochemical modelling of nuclear fuel

Henri Loukusa, Timo Ikonen, Ville Valtavirta, Ville Tulkki
VTT Technical Research Centre of Finland Ltd.
Kivimiehentie 3, PL 1000, 02044 VTT
henri.loukusa@vtt.fi

ABSTRACT

The elemental and chemical composition of nuclear fuel pellets are key factors influencing the material properties of the pellets. The oxidation state of the fuel is one of the most important chemical properties influencing the material properties of the fuel, and it can only be determined with the knowledge of the chemical composition. In this work, the elemental composition of the fuel is obtained from a burnup calculation and the temperature and pressure calculated with a fuel performance code. These can be used in Gibbs energy minimization to calculate chemical properties of nuclear fuel. These include important parameters such as the oxygen potential or partial pressures of reactive gaseous species.

1 INTRODUCTION

Nuclear fuel is the most central part of a nuclear power plant, being the basis of energy production. The cladding containing the pellets is often said to be the first release barrier preventing the release of radioactive material from fuel. The integrity of the cladding must be ensured so that nuclear power plants may be operated safely. The chemical behavior of nuclear fuel influences cladding behavior, especially during pellet-cladding interaction (PCI). Fuel material properties such as heat conductivity, melting point and swelling and of course the release behavior of fission products from the fuel are also affected [1].

The problem of modelling the chemical behaviour of fuel at large scales may be approached through thermodynamics or kinetics. The kinetic calculations require data of the rates on all important individual chemical reactions that could take place in the system. With a complex system such as nuclear fuel the number of possible reactions is overwhelmingly large and suitable data is mostly lacking. In contrast, a thermodynamic approach requires the knowledge of all important species that could occur in the system, and thermodynamic data is available for many chemical species occurring in nuclear fuel. A thermodynamic approach is based on the assumption that the system under consideration is at thermochemical equilibrium. At least regarding the behaviour of some of the more volatile elements

such as iodine or tellurium the equilibrium approximation has been shown to yield results that are quite close to experimental data for these elements measured from irradiated nuclear fuel [2].

Apart from the purely chemical behavior, many other phenomena occur in nuclear fuel -- particularly mass transfer -- and complicate an analysis of the chemistry of nuclear fuel. A simple thermochemical equilibrium calculation can therefore be only used as a first approximation of the chemical state of nuclear fuel. Nevertheless, useful information about the possible behavior of nuclear fuel can be obtained in this way. According to the second law of thermodynamics, an isolated system evolves towards the equilibrium state, so the results from a thermodynamic equilibrium calculation can be used to formulate driving forces for nonequilibrium phenomena such as diffusion.

Gibbs energy minimization is a type of thermochemical equilibrium calculation where only the knowledge of possible species and phases occurring in the system are required, and knowledge of reactions between these species is not needed. The first computer program applying these methods to systems of multiple mixture and pure phases was the SOLGASMIX program by Gunnar Eriksson in the 1970s [3]. Even though Gibbs energy minimization is a powerful tool in the determination of the equilibrium chemical composition of a system, with a large number of possible chemical species and phases the method can be slow. With increasing computing power, the possibility of

investigating nuclear fuel with Gibbs energy minimization has become possible.

Recently, Baurens et al. [2] and Piro et al. [4] demonstrated the application of a full-fledged Gibbs energy minimization program in coupled calculations. Piro et al. coupled a thermochemical calculation with neutronics and thermomechanical calculations, and Baurens et al. used a coupled thermochemical-mechanical simulation to investigate a stress corrosion cracking failure criterion.

A Gibbs energy minimization program has been developed at VTT for the calculation of the chemical state of nuclear fuel, and open source tools such as Thermochemica and OpenCALPHAD are becoming available.

2 METHODOLOGY

2.1 Calculation procedure

In this work, the oxygen potential of a rod measured by Walker et al. [5] is modeled. The rod is from a 15x15 PWR assembly and has been irradiated up to a rod-average burnup of 97.6 MWd/kgU. The thermomechanical behavior of the rod is modeled with the fuel performance code FRAPCON-4.0 and mole amounts of fission products are obtained from a burnup calculation performed with the Monte Carlo neutronics code Serpent. These results are shown in figure 1.

Results from FRAPCON and Serpent are post-processed with MATLAB and used in a Gibbs energy minimization routine to calculate various chemical properties of the fuel. Thermochemical data are obtained from the Royal Military College of Canada nuclear fuel model [6].

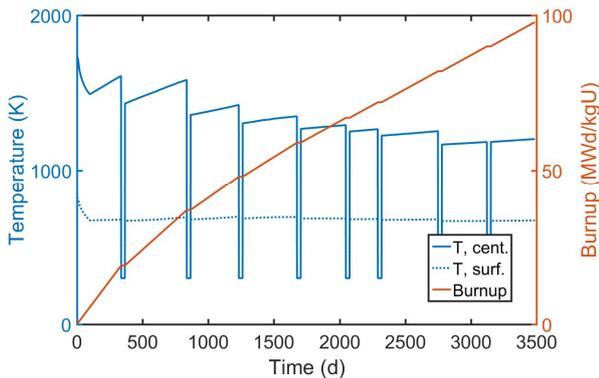


Figure 1: Fuel temperature as calculated by FRAPCON and burnup as calculated by Serpent. [10]

2.2 Gibbs energy minimization

The basic principle of Gibbs energy minimization is based on the fact that in an

isothermal and isobaric system, the minimum of the Gibbs energy of the system corresponds to the thermochemical equilibrium state of the system. The Gibbs energy of the system can be formulated as the sum of the product of the mole amount and chemical potential over each species in each phase of the system. The chemical potential of a species is the partial derivative of Gibbs energy with respect to the mole amount of the species when the mole amounts of all other species are kept constant.

$$G = RT \sum_{\phi=1}^P \sum_{i=1}^{S_{\phi}} n_i^{\phi} \mu_i^{\phi} \quad (1)$$

Here, ϕ is an index over the phases in the system, P , and i an index over the species in a phase, S_{ϕ} . n_i^{ϕ} and μ_i^{ϕ} are the mole amount and the chemical potential of species i in phase ϕ in the system.

The chemical potential of a species is dependent on temperature and pressure. For mixture phases, it is also dependent on the chemical composition of the phase in which the species occurs.

A set of constraints is used to calculate an equilibrium for a given system. These constraints are formed from the amounts of the components, often taken as the elements, of the system. The constraints are formulated as follows:

$$b_j = \sum_{\phi=1}^P \sum_{i=1}^{S_{\phi}} a_{ij}^{\phi} n_i^{\phi}, j = 1, \dots, C \quad (2)$$

Here, C is the number of components in the system and b_j the mole amount of component j . The factor a_{ij} is the stoichiometric coefficient of component j in species i . The mole amounts b_j are then used as constraints for equation (1). An additional constraint is that the mole amounts of species in the system must be positive. This constrained minimization problem can be solved by the application of the Lagrange multiplier method.

3 RESULTS

3.1 Oxygen potential

In figure 2 the oxygen potential calculated at three radial locations is shown as a function of temperature. Walker et al. [5] have measured the oxygen potential from these radial locations at different temperatures. The calculated values are in good agreement with the measured values, and the trend of increasing oxygen potential with increasing radius and also with increasing temperature is clearly visible. As the burnup also increases when moving along the pellet radius from the centerline to the pellet rim, this implies that the oxygen potential increases with increasing burnup.

The oxygen potential for the slightly hyperstoichiometric fresh fuel ($\text{UO}_{2.005}$) as calculated with data from the RMC nuclear fuel model is shown in figure 2. This makes it evident that according to the experimental results the oxygen potential has decreased with burnup from the initial value. From the trend of increasing burnup with pellet radius (and therefore burnup) one may say that even though the oxygen potential must have first decreased, it has then begun to increase again. Only on the pellet rim, where local burnup is very high, is the oxygen potential at almost the value it had as fabricated.

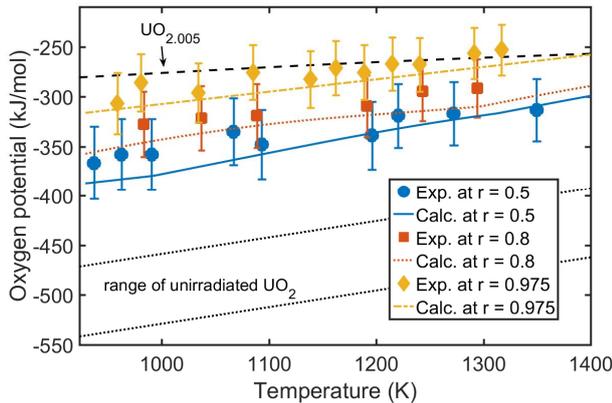


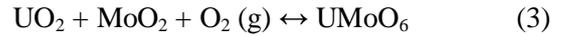
Figure 2: Oxygen potential of fuel at a burnup of 97.6 compared to experimental results by Walker et al. [5]. [10]

Using the local mole amounts and temperatures during the life of the rod, an estimate for the oxygen potential can be calculated at any point in the life of the fuel rod, as is shown in figure 3.

In the first two cycles, the dominating effect is actually the decrease of oxygen potential with burnup only occurs with hyperstoichiometric fuel. The decrease can be seen both in the fuel centerline and on the fuel surface. This can be explained by the uptake of oxygen by various species formed by fission products. It is commonly said that fission products cannot bind all the oxygen released by fission, but this is only partially true. If there is enough oxygen, some fission products can form species in which they occur in a more oxidized form.

During later cycles, the increasing temperature causes increasing oxygen potential with rod-average burnup. At the pellet centerline the changes in the mole amounts of elements with burnup also increase the oxygen potential with burnup. The discontinuities occur at the outages, after which the LHGR and therefore the temperature changes. The oxygen potential at 298 K during the simulated outage is not shown for clarity. The oxygen potential at the pellet surface is quite

constant, due to the buffering effect of UMoO_6 , whereas in the pellet centerline the UMoO_6 species does not form. The reaction



functions as a buffer for oxygen potential according to the calculation, preventing the fuel matrix from oxidizing considerably and maintaining a near-constant oxygen potential at a given temperature.

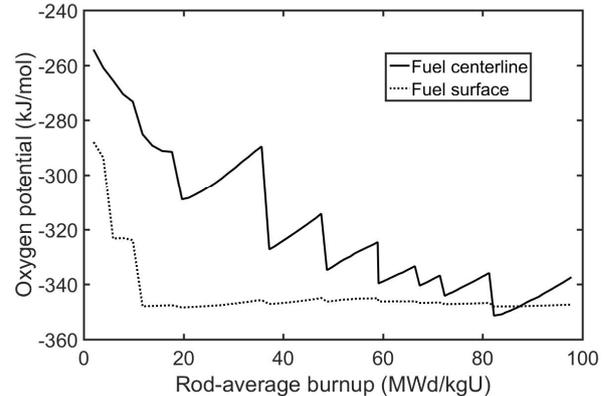


Figure 3: Oxygen potential at fuel centerline and at fuel surface as a function of burnup. [10]

3.2 Partial pressures of reactive gaseous species

Some fission products, such as cesium, iodine and tellurium, are volatile and corrosive to the fuel cladding. Their volatility and reactivity is dependent on their chemical form. For example, iodine is very reactive towards the cladding as atomic and molecular iodine (I and I_2), but unreactive as cesium iodide (CsI). With Gibbs energy minimization, their mole amounts can be easily calculated. For example, Baurens et al. [2] have investigated a possible iodine stress corrosion cracking criterion based on such data.

However, the exact partial pressure of iodine that may cause stress corrosion cracking is still a matter of debate and needs further experimental investigation. Other species than I and I_2 may also contribute to stress corrosion cracking, such as the tellurium species TeI_2 and TeI_4 [2]. Unfortunately, the species TeI_2 is absent from the database used in this work. This may have an effect overall results, as TeI_2 may form in appreciable amounts in irradiated fuel [7].

In figure 4, the calculated partial pressures of some important corrosive species at the fuel surface are shown. It is not surprising that the partial pressures of these species increase with burnup. For reference, the temperatures – apart from the very low burnups – are near 675 K. As can be seen, the largest partial pressure is that of I and I_2 combined.

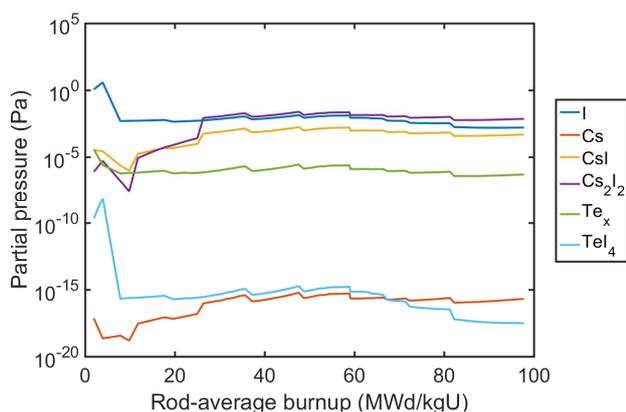


Figure 4: Calculated partial pressures of corrosive species.

However, it has long been known [8] that radiolysis decomposes cesium iodide into cesium and iodine. This kinetic effect should be taken into account when calculating these partial pressures. The application of the immaterial constraint method [9] in this problem should yield more accurate results.

4 CONCLUSIONS

In this work, the use of a Gibbs energy minimization program in modeling nuclear fuel was demonstrated. Even though the assumption of thermochemical equilibrium is difficult to verify, the results calculated with such an assumption were shown to agree with experimental data from nuclear fuel satisfactorily.

The calculated local oxygen potentials can be used in an oxygen diffusion calculation as the driving force of diffusion in future work. The knowledge of the partial pressures of reactive gaseous species are important in determining the probability of failure of fuel cladding by stress corrosion cracking. The thermodynamically calculated values may be refined by the application of the immaterial constraint method in Gibbs energy minimization in future work.

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