



Thermochemical modeling of nuclear fuel and the effects of oxygen potential buffers



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HIGHLIGHTS

- A Gibbs energy minimization routine has been developed for nuclear fuel modeling.
- The initial stoichiometry affects the development of the oxygen potential of fuel.
- UMoO_6 is found to buffer the oxygen potential of nuclear fuel.

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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. A measure of the oxidation state is the oxygen chemical potential of the fuel. It can be buffered by redox pairs, such as the well-known Mo/MoO₂ pair.

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. An estimate of the oxygen potential of fuel is calculated with Gibbs energy minimization. The results are compared against experimental data from the literature. The significance of the UMoO_6 compound and its buffering effect on the oxygen potential is emphasized.

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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 modeling the chemical behavior 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 behavior 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

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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 [3].

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 [4]. 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.

As early as 1986, Imoto [5] calculated the chemical state of fission products in uranium oxide fuel with a simple thermochemical model having a few species and phases. Similar investigations were performed later by Moriyama and Furuya [6]. Both used a variant of SOLGASMIX. The TRAFIC code includes a thermochemical model called Alchemist [7] and a thermochemical model with an equilibrium calculation was implemented in the VICTORIA severe accident code [8]. The MFPR fission product release code developed by Veshchunov et al. [9] implements a thermochemical equilibrium calculation procedure, and has been applied successfully in modeling severe accident test results. Recently, Baurens et al. [2] and Piro et al. [10] 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.

In this work, thermomechanical and neutronics calculations are used with a Gibbs energy minimization program to estimate the chemical composition of nuclear fuel. The results are first validated with a comparison to experimental results by Walker et al. [11] as has been done previously by Piro et al. [10]. The oxygen potential of fuel is the focus of this work, and its background is described in the following section.

2. Oxygen potential of nuclear fuel

In this work, we concentrate on the calculation of the oxygen potential of the fuel. The oxygen chemical potential (often called just the oxygen potential) is related to the oxidation state of a given system. At a constant oxygen potential and varying temperature, the fuel oxidizes or reduces to remain at equilibrium, whereas at a constant oxygen-to-metal ratio of the fuel, the oxygen potential varies with temperature. The oxygen potential is therefore related to the stoichiometry of the fuel. The oxygen potential of the fuel is not determined solely by the uranium dioxide phase, but also by possible secondary phases such as oxides or metallic phases. At equilibrium, the oxygen potential across all phases is the same by the definition of equilibrium. Therefore all the fission products must be taken into account when calculating the fuel oxygen potential, not just those dissolved in the uranium oxide matrix as has previously been done, for example in Ref. [12].

The stoichiometry of the fuel has a significant effect on the thermal conductivity of the fuel, and so influences the temperature distribution in the fuel. The difference in temperature calculated with and without this effect can be as large as 100 K [13]. The oxidation state of the fuel also has a very significant effect on the release of fission products from the fuel: even though the noble

gases do not chemically react with the fuel, their diffusion coefficients depend on the stoichiometry of the fuel [14], whereas other volatile fission products such as tellurium, iodine or cesium also react with their environment and so behave differently in chemically different environments [1,15].

When comparing calculated results with experimental values for oxygen potential, care must be taken to use a suitable value for the oxygen potential. In a typical experimental setup for the measurement of oxygen potential, be it via thermogravimetry or electromotive force (EMF) measurement, the oxygen potential is inferred by measuring the partial pressure of oxygen. In the case of an EMF measurement, the activity calculated from the measured EMF value approximates the partial pressure. In many experimental works the reported oxygen potential is defined as

$$\Delta G_{O_2} = RT \ln p_{O_2} \quad (1)$$

where R is the ideal gas constant and T is the temperature. Piro et al. [16] remind that this definition is incorrect, as the chemical potential of O_2 includes also the standard Gibbs energy of O_2 in addition to the term containing the partial pressure shown above. However, as the value defined by Eq. (1) is usually given in the literature, this is the value reported also in this work.

Only a few references can be found in the literature where the oxygen potential of irradiated stoichiometric or hyperstoichiometric uranium oxide fuel has been measured [11,17–19]. Of the four references where stoichiometric or hyperstoichiometric fuel has been investigated, only Walker et al. [11] give a sufficient amount of data on the tested fuel sample for its behavior to be modeled, such as irradiation history and manufacturing parameters. Therefore the results of Walker et al. are the focus in this work.

Matzke [17,18] reports conflicting results on the behavior of oxygen potential with burnup compared to the others: According to the results by Matzke the oxygen potential is quite low at a high burnup, whereas the results by Walker et al. and Une et al. [19] suggest the oxygen potential increases with burnup. A rim sample analyzed by Matzke [18] had a very high local burnup of 160–200 MWd kg^{−1} and low oxygen potential, but this has been interpreted as the sample having lost a large amount of oxygen to the cladding [20]. Generally, it is thought that oxygen potential increases with burnup.

The oxygen potential of a substance can be buffered by a redox pair, such as a metal and its oxide, and each species participating in the buffering reaction must be present in the system. Most importantly, the reaction must involve gaseous oxygen to have an effect on the oxygen potential, as is apparent from Eq. (1).

Such buffers, termed heterogeneous as they do not occur within a single phase, occur in geochemistry. When the species participating in the buffering reaction are all pure phases, the chemical potential does not change with a change in the mole amount of a component [21]. When at least some of these are solutions, the change in chemical potential is dampened [21]. This means that a buffer presents itself when the chemical potential of oxygen does not increase even though the amount of available oxygen in the system increases. Only after the buffer has been depleted does the oxygen chemical potential increase again.

The Mo/MoO₂ buffer has been suggested previously [17] to buffer the oxygen potential of irradiated fuel. The reaction



functions as the buffer and has a Gibbs energy of reaction between −414 and −403 kJ mol^{−1} at 1023 K depending on the crystal structure of the molybdenum metal being oxidized. The reverse reaction has an equilibrium constant K :

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