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# Thermodynamic considerations and prediction of the primary coolant activity of $^{99}$Tc

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## Abstract

A physical model has been developed to describe the coolant activity behaviour of $^{99}$Tc, during constant and reactor shutdown operations. This analysis accounts for the fission production of technetium and molybdenum, in which their chemical form and volatility is determined by a thermodynamic treatment using Gibbs-energy minimization. The release kinetics are calculated according to the rate-controlling step of diffusional transport in the fuel matrix and vaporization from the fuel-grain surface. Based on several in-reactor tests with defective fuel elements, and as supported by the thermodynamic analysis, the model accounts for the washout of molybdenum from the defective fuel on reactor shutdown. The model also considers the recoil release of both $^{99}$Mo and $^{99}$Tc from uranium contamination, as well as a corrosion source due to activation of $^{98}$Mo. The model has provided an estimate of the activity ratio $^{99}$Tc/$^{137}$Cs in the ion-exchange columns of the Darlington Nuclear Generating Station, i.e., $6 \times 10^{-6}$ (following ~200 days of steady reactor operation) and $4 \times 10^{-6}$ (with reactor shutdown). These results are consistent with that measured by the Battelle Pacific Northwest Laboratories with a mixed-bed resin-sampling device installed in a number of Pressurized Water Reactor and Boiling Water Reactor plants.

## 1. Introduction

Radionuclides such as $^{14}$C, $^{94}$Nb, $^{3}$H, $^{36}$Cl, $^{59}$Ni, $^{99}$Tc, $^{129}$I, $^{79}$Se, and the actinide isotopes of U, Th, Pu, Pa, Am and Np, are of potential interest to the long-term management of low and intermediate level wastes. Most of these radionuclides are difficult-to-measure (DTM) because they are non-gamma emitting and consequently scaling factors are required to estimate their concentrations for reactor waste management. Scaling factors for several radionuclides of interest can be estimated from their activities in the reactor coolant system. Due to the much lower concentrations of many of the DTM radionuclides, e.g., $^{129}$I and $^{99}$Tc, their experimental scaling factor development poses a major challenge and theoretical treatments have been proposed for their estimation [1–3]. The PROFIP code, for instance, has been developed to estimate coolant activity concentrations of fission products and actinides in pressurized water reactors (PWRs) [1]. Similarly, the 3R-STAT code

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focuses on an estimation of $^{129}$I and $^{99}$Tc coolant activities using measured activities of $^{60}$Co, $^{137}$Cs and short-lived radioiodine species [3].

For CANDU reactor analysis, a method has been recently proposed for predicting the coolant activity of the long-lived $^{129}$I, and its scaling factor relative to that of $^{137}$Cs, based on the measured coolant activities of the short-lived iodine species [4]. In this paper, the model is extended for estimation of the coolant activity of the long-lived $^{99}$Tc (half-life of $2.13 \times 10^5$ years). This work involves the computed isothermal phase equilibrium of Mo and Tc in liquid water as portrayed in Pourbaix diagrams, and the volatility of these species in a steam atmosphere with a Gibbs energy minimization procedure [5–7]. Based on insights provided by the thermodynamic analysis, a fission product release model is developed considering the physical mechanisms of release from defective fuel elements and uranium contamination on in-core surfaces [8–16].

## 2. Model development

With defective fuel, there is a breach in the cladding so that primary coolant can enter into the fuel element and fission products can escape through the defect site into the heat-transport system. A thermodynamic analysis is used to describe the leaching behaviour of fission products (i.e., Mo and the daughter product Tc) during reactor shutdown conditions (Section 2.1), and their release behaviour with a steam environment present in the gap during steady reactor operation (Section 2.2). Finally, based on the thermodynamic predictions, and from in-reactor experiments at the Chalk River Laboratories (CRL), a mathematical treatment is developed from mass balance considerations to predict the time-dependent coolant activity behaviour of $^{99}$Tc during constant power operation and for reactor shutdown situations (Section 2.3). This model considers the possibility of fission product release of $^{99}$Mo and $^{99}$Tc from both defective fuel and uranium contamination on in-core surfaces. A possible source of $^{99}$Tc resulting from the corrosion and activation of $^{98}$Mo is also considered.

### *2.1. Thermodynamic analysis for reactor shutdown conditions*

During reactor shutdown, the primary coolant is in the liquid state in the fuel-to-clad gap of a defective element and is therefore in direct contact with the uranium dioxide fuel and any fission products exposed to the free surfaces. The redox potential, $E_h$, and pH are important variables in understanding the isothermal phase equilibrium of a particular element in liquid water, i.e., the phase equilibrium can be represented in a $E_h$-pH space with Pourbaix diagrams [5,6]. These diagrams can in fact be developed more generally with a Gibbs energy minimization procedure, using the Facility for the Analysis of Chemical Thermodynamics (FACT) [7]. This latter approach is capable of considering all of the candidate chemical species of a particular element (e.g., U) potentially dissolved (e.g., $UO_2^{2+}, \ldots$) or in contact with water (e.g., $U_4O_9, \ldots$).

For instance, consider the formation of all possible U–H–O species from a mole of U in its most stable allotropic form (orthorhombic) at a given temperature using a minimization procedure. The formation reactions are balanced using only $H_2O$, $H^+$ and $e^-$. These reactions are listed in Table 1 with the standard Gibbs energy changes (i.e., at $E_h$ (S.H.E.) = 0, pH = 0 and molality $m$ (activity) = 1) for 298 and 523 K. To build a Pourbaix diagram over the desired range of $E_h$ and pH, adjustments are made to the standard Gibbs energies in Table 1 to reflect departure from the standard state condition. The steps in the incremental changes of $E_h$ and pH are conveniently made the same. At each step, the Gibbs energies in Table 1 are adjusted by the following change in Gibbs energy:

$$\Delta G_{H^+} = -2.303RT \text{ pH}, \tag{1}$$

$$\Delta G_{e^-} = -\Im E_h, \tag{2}$$

where $\Im$ is the Faraday constant, $R$ is the ideal gas constant and $T$ is the absolute temperature. For the treatment of the 'electron', the symbol '$e^-$' represents an unspecified process in the water phase that controls the redox potential, e.g., dissolved oxygen:

$$1/2\,O_2 + 2H^+ + 2e^- = H_2O. \tag{3}$$

When Eq. (2) is used, one is in effect finding the Gibbs energy change for a process such as Eq. (3) for some particular dissolved oxygen concentration and pH, which determines $E_h$ at that temperature. Pourbaix diagrams generally show the influence of concentration of aqueous species, which has the effect of enlarging the aqueous domains as dilution increases. This aspect of diagram development involves adjusting the Gibbs energies in Table 1 (per mole of U-containing ion) by ($RT\ln m$) (very nearly the thermodynamic activity in dilute solutions). With all Gibbs energies in Table 1 adjusted for concentration, $E_h$ and pH, the lowest value is then found. This identifies the particular U-containing species that is most stable. By repetition of this process for each $E_h$-pH point on the diagram, the domains of the different species can be established.

#### *2.1.1. Pourbaix diagrams for Uranium*

The Uranium Pourbaix diagram at 298 K covering the range of redox potential pertinent to fuel oxidation is shown in Fig. 1. The data for $UO_2$, $U_4O_9$, $U_3O_7$ and $U_3O_8$ is the same as that used for the U–O binary phase diagram [17]. Placed on the diagram for reference are dashed lines ⓐ and ⓑ corresponding to redox potentials