# MODELLING THE ACTIVITY OF $^{99}$Tc IN THE PRIMARY HEAT TRANSPORT SYSTEM OF A CANDU REACTOR

B.J. Lewis and W.T. Thompson
Department of Chemistry and Chemical Engineering
Royal Military College of Canada, PO Box 17000, Kingston, Ontario K7K 7B4

A. Husain
Kinectrics Inc., 800 Kipling Avenue, Toronto, Ontario M8Z 6C4

## 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 a 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 d 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 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.

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.[1] In this paper, the model is extended for estimation of the coolant activity of the long-lived $^{99}$Tc (half-life of $2.13 \times 10^{5}$ y) by considering the physical mechanisms of release from defective fuel elements and uranium contamination on in-core surfaces.

## 2. MODEL DEVELOPMENT

A thermodynamic analysis, based on a Gibbs-energy minimization, was carried out with the Facility for the Analysis of Chemical Thermodynamics (FACT) in order to determine the speciation of the Mo and Tc fission products.[2] This analysis was performed on the basis of a Bruce fuel channel. In particular, the analysis considered the fission product inventory in the fuel bundles of the channel (i.e., as estimated with the ORIGEN code at a fuel burnup of 100 MWh/kgU),[3] and the relative volumes of the fuel bundles to free space in the channel for the atmospheric constituent. This approach essentially assumes an unlimited supply of steam and water into the fuel-to-clad gap where there is an open system with the possibility of a continual replenishment of steam/water from the primary coolant into the failed rod. The details of the calculation are given in Ref. 4.

Figure 1 shows the predicted partial pressures $p_{\mathrm{Tc}}$ and $p_{\mathrm{Mo}}$ for the elements of Tc and Mo. Due to the higher volatility for Mo, the release from the fuel matrix to the fuel-to-clad gap will be dominated solely by this precursor product. The dominant gaseous compound for this species is MoOH over the typical operating temperatures (i.e., ~ 400°C to 2800°C), and system pressure (100 atm), in the presence of steam in the defective fuel rod. However, the Mo partial pressure is significantly reduced at the cooler fuel surface where it will be present as a condensed solid phase (i.e., $MoO_2$ and $Cs_2MoO_4$). The thermodynamic analysis further indicates that Tc will not be released from the water-filled gap on shutdown. On the other hand, Mo is readily soluble under aqueous conditions so that it will be rapidly washed out of the defective rod as $MoO_4^{2-}$. In fact, these predictions are consistent with observations from experimental loop irradiations at the Chalk River Laboratories (CRL) with defective fuel rods.[5] In addition, leaching experiments were performed on spent CANDU rods to measure the combined gap and grain-boundary inventories of $^{137}$Cs, $^{129}$I, $^{90}$Sr, $^{99}$Tc and $^{14}$C, which suggested that technetium is not a volatile species and was unlikely to be found in the gap.[6] It was further suggested that the diffusion coefficient for Tc is considerably smaller than that of Xe, Cs or I.[6,7] Moreover, in agreement with the FACT thermodynamic analysis,[8] it is further noted that Tc will be found as metallic precipitates (with Mo, Ru, Rh and Pd) on the grain boundaries and as metallic alloy inclusions.[9,10,11]

Hence, it is assumed that Mo is released from the defective fuel rod as a result of washout during reactor shutdown/startup but it is not released under dry steam conditions during steady reactor operation. The gap inventory develops from: (i) solid-state diffusion through the solid matrix, and (ii) vaporization from the fuel grain surface with gas-phase transport through the tunnel interlinkage. The release kinetics are therefore controlled by the rate-limiting step between these two processes. The Mo that eventually reaches the gap will be stored there (i.e., as a condensed phase) until the occurrence of a transient event. Technetium that is produced in the gap by the decay of Mo is not mobile. This treatment is also in agreement with that proposed by Vance for the 3R-STAT model, where no Tc source release is assumed to occur from the defective rod itself.[12] On the other hand, both Mo and Tc may be directly released by a recoil fission process from uranium contamination that is deposited on in-core piping surfaces.

### 2.1 Fission Product Release Model

For the relatively short-lived $^{99}$Mo (half-life of 66.02 h), an equilibrium situation is quickly reached so that the release rate for diffusion $R_{dif}$ (atom s$^{-1}$) from the fuel matrix to the fuel-to-clad gap is given by the steady-state relation:[1]

$$R_{dif} = 3\left[\frac{1}{\sqrt{\mu}}\coth\sqrt{\mu} - \frac{1}{\mu}\right]Fy \approx 3\sqrt{\frac{D'}{\lambda}}Fy \tag{1}$$

where $\mu = \lambda/D'$, $\lambda$ is the decay constant, $F$ is the fission rate (fission s$^{-1}$) and $y$ is the cumulative fission yield for $^{99}$Mo. The empirical diffusion coefficient $D'$ (s$^{-1}$) in the fuel matrix can be obtained from a correlation developed from in-reactor loop experiments with defective CANDU fuel rods operating at a linear power $P$ (kW/m):[13]

$$D'_{Iodine} = 10^{9.857\log P - 25.1314} \tag{2}$$

This result can be used since it has been shown in high-temperature annealing experiments that I, Cs, Kr, Xe and Mo have similar diffusivities.[3,14]

The release rate for vaporization $R_{vap}$ (atom $s^{-1}$) can be derived from a mass-transfer model based on the Fick's law of diffusion:[4]

$$R_{vap} = \gamma \, S_{eff} N_A k_{im} \left( \overline{x}^{gs} - x^g \right) \tag{3}$$

where $\gamma (= 1)$ is the number of atoms per molecule of the dominant volatile compound for Mo (i.e., MoOH), $S_{eff}$ is the effective grain-boundary surface area exposed to the gap ($m^2$), $D_{AB}$ is the binary diffusion coefficient ($m^2 \, s^{-1}$) for Mo diffusing in a continuum steam medium, $\overline{x}^{gs}$ is the average mole fraction of the Mo-bearing gaseous compound at the grain surface, $x^g$ is the mole fraction in the gap (~ 0) and $N_A$ is Avogadro's number. The mass transfer coefficient $k_{im}$ (mol $m^{-2} \, s^{-1}$) is defined as:

$$k_{im} = \frac{cD_{AB}}{\ell} \tag{4}$$

where $\ell$ is a characteristic transport-path length through the tunnel interlinkage to the gap (m) (which is approximately equal to the pellet radius), $c = p_T/RT$ is the total molar concentration of gas in the tunnel interlinkage, $p_T$ is the total system pressure (= 100 atm), $R$ is the ideal gas constant and $T$ is the average fuel temperature. The mole fraction $\overline{x}_{Mo}^{gs} = \overline{p}_{Mo} / p_T$ can be estimated by averaging the Mo partial pressures in Fig. 1 over the fuel pellet volume using a given temperature profile for the defective fuel element.[15]

## 2.2 $^{99}$Tc Coolant Activity

The overall release rate from the fuel matrix into the gap is therefore taken as the rate-determining step between solid-state diffusion to the fuel grain surface ($R_{dif}$) and vaporization from the grain surface ($R_{vap}$). For a defective element operating under normal conditions at low (25 kW/m) and high power (52 kW/m), it is shown in Ref. 4 using Eqs. (1) and (3) that diffusion is the rate-limiting step for Mo release into the gap. Hence, $^{99}$Mo will diffuse into the fuel-to-clad gap via Eq. (1), where it is stored during the steady operating period. Consequently, from the mass balance, the steady-state activity in the gap is $A_{go} = R_{dif}$. On a subsequent reactor shutdown, this stored activity is quickly released into the primary heat transport system (PHTS) according to:[4]

$$A_c(t) = \left[ A_{co} + A_{go} \right] e^{-(\lambda + \beta_{S/D})t} \tag{5}$$

where $A_c(t)$ is the coolant activity of $^{99}$Mo at time $t$ following a shutdown, $\beta_{S/D}$ is the purification constant during shutdown and $A_{co}$ is the initial coolant activity at the time of shutdown. This latter contribution is developed during the previous steady operating period from the tramp uranium contamination (Section 2.2.1) or through activation of the corrosion product, $^{98}$Mo (Section 2.2.2). Thus, Eq. (5) yields a source release of $^{99}$Mo into the coolant which will decay into the daughter product, $^{99}$Tc (Section 2.2.3).

### 2.2.1 *Tramp Uranium Release*

Uranium contamination resulting from a previous fuel loss from defective fuel rods or from the fuel manufacturing process can lead to a continual source of fission product release into the PHTS during steady reactor operation when this contamination is deposited on in-core surfaces.

Such contamination is in the form of fine fuel debris, and therefore the temperature generated by fission heating is generally too low for diffusion to be an important transport process. In this case, direct recoil becomes the dominant release mechanism where the release rate $R_{rec}$ (atom $s^{-1}$) for the given isotopes of interest from a small particle deposited on an underlying surface is:[1]

$$R_{rec} = \tfrac{1}{2} F_t y \qquad \textbf{(6)}$$

where $y$ is the fission yield. The tramp uranium fission rate, $F_t$, can be estimated from a coolant-activity analysis of the short-lived radioiodine species based on the methodology detailed in Ref. 1.

### 2.2.2 *Production of $^{99}$Mo by Activation*

The alloys used in the plant piping systems and components (i.e., end fittings, feeder and pressure tubes) are subject to corrosion by the reactor coolant. Some of these corrosion products may be transported in-core where they can become activated by the neutron flux. For instance, this results in the production of such radionuclides as $^{60}$Co and $^{99}$Mo due to activation of the corrosion products, $^{59}$Co and $^{98}$Mo.

As considered in the RADSOURCE Code,[16] the production rate of $^{99}$Mo by activation can be estimated from the measured activity of $^{60}$Co in the PHTS ($A^{60}_{c,meas}$ (Bq)):[4]

$$R^{Mo-99}_{act} = r\left(\frac{\sigma^{98}}{\sigma^{59}}\right)\left(\frac{\lambda^{60}+\beta^{Co}}{\lambda^{60}}\right)A^{60}_{c,meas} \qquad \textbf{(7)}$$

where $\sigma^{98}$ is the microscopic thermal absorption cross section for $^{98}$Mo (= 130 mb at 0.0253 eV), $\sigma^{59}$ is the microscopic thermal absorption cross section for $^{59}$Co (= 37.18 b at 0.0253 eV), $\lambda^{60}$ is the radioactive decay constant for $^{60}$Co and $\beta^{Co}$ is the coolant purification rate constant for Co removal. The ratio $r$ of the number of atoms of $^{98}$Mo/$^{59}$Co can be estimated from the material composition in the pressure tube (i.e., Mo/Co = 25 ppm/10 ppm) and end-fitting body (Stainless Steel 403) (i.e., Mo/Co =500 ppm/90 ppm). Thus, accounting for an isotopic abundance of 24.1% for $^{98}$Mo, $r \sim 1$.

### 2.2.3 *Coolant Activity Mass Balance*

The mass balance for $^{99}$Mo and $^{99}$Tc in the coolant during steady reactor operation (i.e., assuming steady-state conditions for the short-lived $^{99m}$Tc) is therefore given by:[4]

$$\frac{dN^{Mo-99}_{c}}{dt} = R^{Mo-99} - \left(\lambda^{Mo-99} + \beta^{Mo}\right)N^{Mo-99}_{c} \qquad \textbf{(8a)}$$

$$\frac{dN^{Tc-99}_{c}}{dt} = R^{Tc-99} + \lambda^{Mo-99} N^{Mo-99}_{c} - \beta^{Tc} N^{Tc-99}_{c} \qquad \textbf{(8b)}$$

where the following source release rates (i.e., for recoil and activation processes) are defined via Eqs. (6) and (7):

$$R^{Mo-99} = \tfrac{1}{2} F_t y^{Mo-99} + R_{act}^{Mo-99} \qquad \textbf{(9a)}$$

$$R^{Tc-99} = \tfrac{1}{2} F_t \left( y^{d,Tc-99m} + y^{d,Tc-99} \right) \qquad \textbf{(9b)}$$

and $y^d$ is the direct yield, $y$ is the cumulative yield and $\beta$ is the coolant purification constant. The coolant activities for $^{99}$Mo and $^{99}$Tc follow on solution of Eq. (8):

$$A_c^{Mo-99}(t) = A_{co}^{Mo-99} e^{-\left(\lambda^{Mo-99} + \beta^{Mo}\right)t} + \left( \frac{\lambda^{Mo-99}}{\lambda^{Mo-99} + \beta^{Mo}} \right) R^{Mo-99} \left[ 1 - e^{-\left(\lambda^{Mo-99} + \beta^{Mo}\right)t} \right] \qquad \textbf{(10)}$$

and

$$\begin{aligned} A_c^{Tc-99}(t) = {} & A_{co}^{Tc-99} e^{-\beta^{Tc}t} + \Bigg\{ R^{Tc-99} + \left( \frac{\lambda^{Mo-99}}{\lambda^{Mo-99} + \beta^{Mo}} \right) R^{Mo-99} \Bigg\} \left( \frac{\lambda^{Tc-99}}{\beta^{Tc}} \right) \left[ 1 - e^{-\beta^{Tc}t} \right] + \\ & \Bigg\{ A_{co}^{Mo-99} - \left( \frac{\lambda^{Mo-99}}{\lambda^{Mo-99} + \beta^{Mo}} \right) R^{Mo-99} \Bigg\} \left( \frac{\lambda^{Tc-99}}{\lambda^{Mo-99} + \beta^{Mo} - \beta^{Tc}} \right) \left[ e^{-(\lambda^{Mo-99} + \beta^{Mo})t} - e^{-\beta^{Tc}t} \right] \end{aligned} \qquad \textbf{(11)}$$

Here, $A_{co}^{Mo-99}$ and $A_{co}^{Tc-99}$ are the initial activities of $^{99}$Mo and $^{99}$Tc at the start of the irradiation period.

Finally, the coolant activities of $^{99}$Mo and $^{99}$Tc after shutdown (S/D) are given by:[4]

$$A_{S/D}^{Mo-99}(t) = A_o^{Mo-99} e^{-(\lambda^{Mo-99} + \beta_{S/D}^{Mo})t} \qquad \textbf{(12)}$$

and

$$\begin{aligned} A_{S/D}^{Tc-99}(t) = {} & A_o^{Tc-99} e^{-\left(\lambda^{Tc-99} + \beta_{S/D}^{Tc}\right)t} + \left(1 - f^{Mo-99}\right) A_o^{Mo-99} \left( \frac{\lambda^{Tc-99}}{\left(\lambda^{Mo-99} - \lambda^{Tc-99}\right) + \left(\beta_{S/D}^{Mo} - \beta_{S/D}^{Tc}\right)} \right) \times \\ & \left[ e^{-\left(\lambda^{Tc-99} + \beta_{S/D}^{Tc}\right)t} - e^{-\left(\lambda^{Mo-99} + \beta_{S/D}^{Mo}\right)t} \right] + A_o^{Tc-99m} \left( \frac{\lambda^{Tc-99}}{\lambda^{Tc-99m} - \lambda^{Tc-99}} \right) \left[ e^{-\left(\lambda^{Tc-99} + \beta_{S/D}^{Tc}\right)t} - e^{-\left(\lambda^{Tc-99m} + \beta_{S/D}^{Tc}\right)t} \right] + \\ & \left( \frac{\lambda^{Tc-99m} f^{Mo-99} A_o^{Mo-99}}{\left(\lambda^{Mo-99} - \lambda^{Tc-99m}\right) + \left(\beta_{S/D}^{Mo} - \beta_{S/D}^{Tc}\right)} \right) \Bigg\{ \left( \frac{\lambda^{Tc-99}}{\lambda^{Tc-99m} - \lambda^{Tc-99}} \right) \left[ e^{-\left(\lambda^{Tc-99} + \beta_{S/D}^{Tc}\right)t} - e^{-\left(\lambda^{Tc-99m} + \beta_{S/D}^{Tc}\right)t} \right] + \\ & \left( \frac{\lambda^{Tc-99}}{\left(\lambda^{Mo-99} - \lambda^{Tc-99}\right) + \left(\beta_{S/D}^{Mo} - \beta_{S/D}^{Tc}\right)} \right) \left[ e^{-\left(\lambda^{Mo-99} + \beta_{S/D}^{Mo}\right)t} - e^{-\left(\lambda^{Tc-99} + \beta_{S/D}^{Tc}\right)t} \right] \Bigg\} \end{aligned} \qquad \textbf{(13)}$$

Here the term $A_o^{Mo-99} = A_{co}^{Mo-99} + A_{go}^{Mo-99}$ accounts for both the steady-state and shutdown (i.e.., washout) source of $^{99}$Mo, and

$$A_o^{Tc-99m} = \left( \frac{\lambda^{Tc-99m}}{\lambda^{Tc-99m} + \beta^{Tc}} \right) \left[ \tfrac{1}{2} F_t y^{d,Tc-99m} + f^{Mo-99} R^{Mo-99} \left( \frac{\lambda^{Mo-99}}{\lambda^{Mo-99} + \beta^{Mo}} \right) \right] \qquad \textbf{(14)}$$

where $f^{Mo-99} = 0.88$ is the branching fraction from $^{99}$Mo to $^{99m}$Tc. For an operating period of duration $t = t^*$, $A_{co}^{Mo-99} = A_c^{Mo-99}(t = t^*)$, $A_{go}^{Mo-99} = R_{dif}$ and $A_o^{Tc-99} = A_c^{Tc-99}(t = t^*)$, i.e., as evaluated from Eqs. (10), (1) and (11), respectively.

## 3. DISCUSSION

### 3.1 Example Calculation

Based on a coolant activity analysis of the short-lived iodine isotopes observed in the Darlington Nuclear Generating Station (DNGS), the corresponding coolant activity behaviour for technetium can be estimated using the model parameters derived in this analysis.[1] In particular, this previous analysis indicates that there is a single defective rod operating at 40 kW/m ($F_f = 6.0 \times 10^{14}$ fission s$^{-1}$), with a tramp uranium fission rate of $F_t = 3.6 \times 10^{12}$ fission s$^{-1}$.[1] Thus, the coolant activity concentrations of $^{99}$Mo and $^{99}$Tc can be predicted as a function of time with Eqs. (10), (11), (12) and (13) for a steady period of reactor operation of $t \sim 200$ d followed by a reactor shutdown. This calculation assumes that the coolant activities of $^{99}$Mo and $^{99}$Tc are initially zero. The average value of the measured $^{60}$Co coolant activities in the DNGS (i.e., 0.12 μCi kg$^{-1}$) can be further used to estimate the $^{99}$Mo production by activation with $\beta_{\mathrm{Co}} \sim \beta_{\mathrm{I}}$. Moreover, the empirical diffusion coefficient for Mo, as well as the purification constants for Mo and Tc, can be taken equal to that obtained for the iodine analysis in Ref. 1, where $D'_{\mathrm{Mo}} = D'_{\mathrm{I}} = 4.0 \times 10^{-10}$ s$^{-1}$ and $\beta_{\mathrm{Mo}} = \beta_{\mathrm{Tc}} = \beta_{\mathrm{I}} \sim 4 \times 10^{-5}$ s$^{-1}$. These latter coefficients are further assumed to be the same for both steady reactor operation and shutdown (so that $\beta = \beta_{\mathrm{S/D}}$).

From a waste characterization perspective, it is also useful to compare these concentrations against those for the easy-to-measure radionuclide, $^{137}$Cs. For instance, the corresponding activity that develops in the coolant during a constant operating period for $^{137}$Cs can be evaluated from:[4]

$$A_c(t) = \mu F_f y \left\{ \frac{1-e^{-\phi\tau}}{\phi} + \left( \frac{e^{-\psi\tau} - e^{-\phi\tau}}{(\psi - \phi)} \right) \frac{3}{\psi} \left[ 1 - \sqrt{\psi} \cot \sqrt{\psi} \right] + 6\psi \sum_{n=1}^{\infty} \left( \frac{e^{-\phi\tau} - e^{-n^2\pi^2\tau}}{n^2\pi^2 (n^2\pi^2 - \psi)(n^2\pi^2 - \phi)} \right) \right\} + \lambda y \left( \frac{1-e^{-\phi\tau}}{\beta} \right) \left( \tfrac{1}{2} F_t \right) \qquad \textbf{(15)}$$

where $\psi = \nu / D'$, $\phi = \beta / D'$ and $\tau = D't$. Since both molybdenum and cesium also exhibit a spiking behaviour during reactor shutdown, the cesium spike release can similarly be evaluated from Eq. (5). Here the initial coolant activity at the time of shutdown, which is present from the previous period operation of time $t^*$, can be evaluated from Eq. (15) as $A_{co}^{Cs-137} = A_c^{Cs-137}(t = t^*)$. The stored gap activity that also develops during this irradiation period for $^{137}$Cs is:

$$A_{go}^{Cs-137} = \left[ \frac{\left(1 - e^{-\psi\tau}\right)}{\psi} - 6 \sum_{n=1}^{\infty} \frac{e^{-\psi\tau} - e^{-n^2\pi^2\tau}}{n^2\pi^2 \left(n^2\pi^2 - \psi\right)} \right] \mu F_f y \qquad \textbf{(16)}$$

Thus, the steady state and shutdown activities for $^{137}$Cs can be calculated from Eqs. (15), (16) and (5) where $D'_{\mathrm{Cs}} = 4.0 \times 10^{-10}$ s$^{-1}$, $\nu_{\mathrm{Cs}} = 1.32 \times 10^{-7}$ s$^{-1}$and $\beta_{\mathrm{Cs}} = 4 \times 10^{-6}$ s$^{-1}$.[1]

The results of this analysis are shown in Fig. 2(a). Since no isotopes of $^{99}$Mo and $^{99}$Tc are released from defective fuel during steady reactor operation, the contributions from these isotopes to the coolant activity in Fig. 2(a) correspond to that for tramp uranium only. The $^{99}$Mo is also produced by activation of the corrosion product $^{98}$Mo. Hence, these results also apply to the situation when no defective fuel is present. As further shown in Fig. 2(a), all coolant activity contributions that do not result from defective fuel quickly reach an equilibrium state for the given purification constant. On the other hand, there is a continual buildup of the total coolant activity of $^{137}$Cs. This continuous activity increase is due to release from the defective rod where there is an on-going production of cesium in the fuel matrix, which diffuses into the fuel-to-clad gap and eventually into the coolant through the breached site. This contribution is in addition to that released from the tramp uranium. On shutdown, as shown in Fig. 2(b), the activity that has been stored in the (steam-filled) gap during steady operations is quickly washed out of the defective rod, resulting in a spike of activity for both $^{137}$Cs and $^{99}$Mo. Consequently, the coolant activity of the daughter radionuclide $^{99}$Tc increases as a result of the decay of the Mo activity spike.

## 3.2 Predicted Scaling Ratio for $^{99}$Tc/$^{137}$Cs

The radionuclide activities will accumulate on the ion-exchange (I-X) columns with continuous coolant cleanup during steady reactor operations and following reactor shutdown.
Thus, one can integrate over the corresponding curves in Fig. 2(a). Hence, the scaling ratio for $^{99}$Tc/$^{137}$Cs is $5.8 \times 10^{-6}$, which is based on the accumulated isotopic activities on the I-X columns over 200 d of steady operation.[4] On the other hand, if defective fuel had not been present, the accumulated activity for $^{137}$Cs in the above expression would have only been 0.0411 μCi/kg (i.e., instead of 1.35 μCi/kg), reflecting the tramp uranium contribution. In this case, the scaling ratio would increase by about a factor of 30 yielding a value of $1.9 \times 10^{-4}$. In fact, a single sample from the PHTS resins at the DNGS yielded a measured activity ratio for $^{99}$Tc/$^{137}$Cs of $2 \times 10^{-4}$.

The previous analysis only considered the calculation of a scaling ratio that would arise during steady operation and neglected the effect of any augmented release due to washout on shutdown. Thus, as follows from Fig. 2(b), a ratio of $3.5 \times 10^{-6}$ is obtained which is similar to that previously determined for steady operations (i.e., $5.8 \times 10^{-6}$). This result is to be expected since cesium, as well as the precursor of technetium (i.e., molybdenum), both exhibit a similar spiking behaviour on shutdown. These ratios for the CANDU reactor can now be compared to that observed in pressurized and boiling water reactors (see Section 3.3).

## 3.3. Comparison to Measured Scaling Ratios for $^{99}$Tc/$^{137}$Cs

The Battelle Pacific Northwest Laboratories designed a mixed-bed test resin sampling device to simulate a scaled-down version of the purification demineralizer system for a nuclear power plant.[16] These sampling devices were installed at 10 Pressurized Water Reactors (PWR) and 7 Boiling Water Reactors (BWR). The devices were operated with scaled-down flow rates to simulate the cleanup of the reactor coolant (i.e., ~80 mL/min for periods ranging from several days to as long as 6 weeks in the PWR tests and ~42 mL/min for 48 h in the BWR tests). This period of operation is considerably shorter than normal operating times of full-scale purification demineralizer beds (i.e., which are typically employed for up to one year in PWRs). The length of the test resin columns (30 cm) were also relatively short compared to the 90-120 cm deep beds used at PWR stations. The simulated BWR powdered test resins were also operated for considerably less time than actual operations. Radioanalytical techniques were used to measure the concentrations of $^{129}$I, $^{99}$Tc, $^{90}$Sr, $^{238}$Pu, $^{239}$Pu, $^{240}$Pu and $^{14}$C. In particular, inductively-coupled plasma mass spectrometry (ICPMS), with either a electrothermal vaporization graphite furnace or ultrasonic nebulizer, were used to determine the distributions of $^{99}$Tc on the resin columns. Also other gamma emitting radionuclides were measured by gamma spectrometry.

$^{99}$Tc/$^{137}$Cs ratios can be obtained from the available concentration measurements for the various plant test resin columns.[16] These ratios increase with the number of days sampled in the PWR tests, i.e., the isotopic ratio ranged from $3.5 \times 10^{-9}$ (0.083 sampling days) to $1.8 \times 10^{-6}$ (40 sampling days). In comparison, the observed ratio in the BWR tests was several orders of magnitude larger which ranged from $8.5 \times 10^{-6}$ to $6.6 \times 10^{-3}$.

These ratios can be compared to the current analysis performed for the DNGS in Section 3.2, although it is recognized that the activation contribution may differ vastly between different plant designs. Since the Battelle sample devices were installed during steady-state conditions, the steady operation ratio of $5.8 \times 10^{-6}$ for the DNGS should apply. However, as already mentioned, there is little difference in this ratio with that for shutdown. In fact, the DNGS ratio is within the range of that measured for the PWR and BWR plants. The operation of CANDU reactors would be closer to that of PWRs where no boiling occurs. In fact, the predicted ratio for the DNGS is in reasonable agreement (factor of 3) with that for the PWR Indian Point-2 plant (which had the longest sampling test).[16] However, it is recognized that the PWR and BWR fuel operate to considerably longer burnups (i.e., ~1000 MWh/kgU versus 180 MWh/kgU) and have much lower heat ratings (20 kW/m versus 40 kW/m). Longer fuel burnups will increase the production of $^{137}$Cs in the defective rods but will not influence the amount of $^{99}$Mo in the fuel (which will reach equilibrium within ~10 d). Hence, this effect will result in a lower observed $^{99}$Tc/$^{137}$Cs ratio for the light water plants where there is an increased cesium inventory in the coolant but a relatively unchanged amount of technetium (via the decay of the molybdenum that is released from the defective rod). In addition, the effect of deposition of fission products (i.e., Mo and Tc) in the PHTS of the CANDU reactor has been conservatively ignored in the model. The materials are also slightly different in the various reactors, which will affect the activation contribution from the corrosion of $^{98}$Mo. BWR plants would presumably experience much greater corrosion rates due to boiling (and perhaps have a smaller release of water-soluble cesium from defective fuel during steady operation). Hence, these effects would result in much higher scaling ratios for the BWR plants as in fact observed. Thus, the current analysis for the CANDU station appears to be consistent with the observed scaling ratios in the PWR and BWR plants, although it is clear that $^{99}$Tc measurements are needed for model validation for the CANDU analysis.

## 4. CONCLUSIONS

A model has been developed to estimate the long-lived $^{99}$Tc coolant activity as a function time for constant reactor operation and during reactor shutdown. The current model accounts for the physical processes of release from the fuel matrix via a rate-determining step of solid state diffusion to the grain surface and vaporization from this surface into the free spaces within the defective rod where steam is present. The model further accounts for a production of technetium due to the washout of the parent molybdenum species from defective CANDU fuel rods on reactor shutdown. The direct release of technetium from tramp uranium contamination on in-core surfaces is also considered as a continual source of release into the reactor coolant. In addition, the production of technetium from the corrosion and activation of stable molybdenum is estimated in accordance with the measured coolant activity behaviour of $^{60}$Co. The resulting activity in the PHTS, and as contained on the ion-exchange columns, is evaluated from mass-balance considerations taking into account the various sources and a loss due to coolant cleanup operations.

A coolant activity analysis of the short-lived iodine species and long-lived $^{137}$Cs isotope, as observed in the Darlington Nuclear Generation Station, has been used to provide the relevant transport parameters for prediction of the coolant inventories of $^{137}$Cs and $^{99}$Tc. The sample calculation for the DNGS yields a scaling ratio for $^{99}$Tc/$^{137}$Cs of $6 \times 10^{-6}$ after ~200 d of steady reactor operation with a single defective fuel rod operating at 40 kW/m. A similar value of $4 \times 10^{-6}$ is obtained following reactor shutdown with continuous coolant cleanup. This predicted value is consistent with measured coolant activity ratios obtained in test resin samples from pressurized water reactors ($4 \times 10^{-9}$ to $2 \times 10^{-6}$) and boiling water reactors ($9 \times 10^{-6}$ to $7 \times 10^{-3}$) in a study by the Battelle Pacific Northwest Laboratories. However, $^{99}$Tc data for the CANDU reactor are still required for model validation due to inherent differences in the reactor and fuel designs between the light water and CANDU reactors.

## 5. ACKNOWLEDGEMENTS

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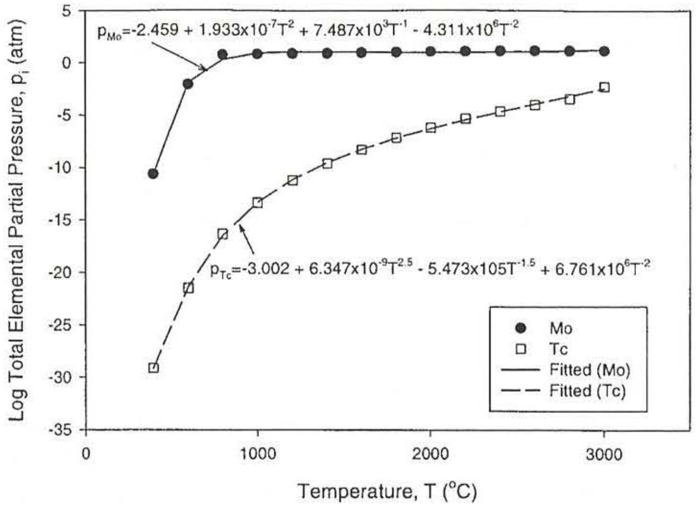

**Figure 1.** Variation of partial pressure of Mo and Tc with temperature.

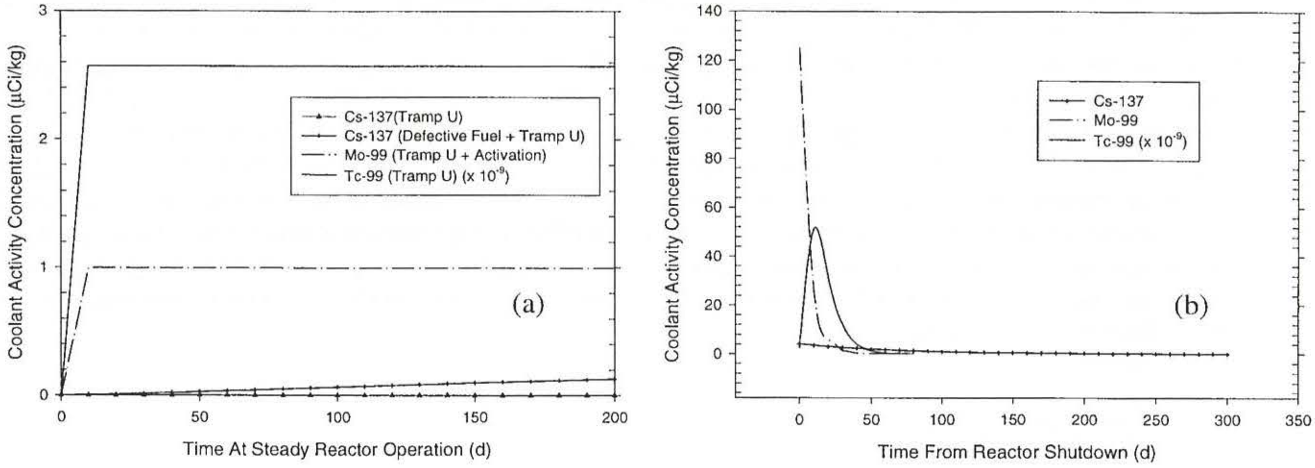

**Figure 2.** Coolant activity concentrations of various isotopes for (a) steady reactor operation and (b) followed by a reactor shutdown. The initial coolant activity concentrations of $^{137}$Cs and $^{99}$Mo at the time of shutdown in (b) are derived from the steady state values in (a) plus that acquired from the spike release.