

The Dissolution and Transport of Radionuclides from Used Nuclear Fuel in an Underground Repository

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Abstract: The Canadian deep geologic repository concept for used nuclear fuel consists of used fuel bundles placed in durable containers and emplaced within rooms excavated deep in a stable geological formation. In the event of container failure, the rate of migration of radionuclides to the surface biosphere is limited by the rate of nuclide release from the fuel matrix and by nuclide transport through multiple engineered and geological barriers. COMSOL was used to: first, model the dissolution of the used fuel matrix as a function of alpha, beta and gamma dose rates and study the release of radionuclides from a pin-hole defect in the container wall, and second to verify an existing safety assessment model. Nuclide migration via diffusive transport through the engineered barrier system in the near field was computed, and the results compared to analytical solutions and to the safety assessment model.

Keywords: Nuclear, Used-fuel Repository, Near-Field

1. Introduction

The Canadian deep geologic repository concept for used nuclear fuel consists of used fuel bundles placed in durable containers which are emplaced within vaults excavated deep in a stable geological formation and surrounded by self-sealing clay-based materials (Garisto et al., 2009a). This concept is similar to that considered by other countries for their high-level wastes, and provides multiple, independent, passive barriers for isolating and retaining the radionuclides.

The current repository concept is designed to hold between 3.6 and 7.2 million CANDU fuel bundles in approximately 10,000 – 20,000 containers. The container has a corrosion resistant outer copper shell with a steel inner vessel for structural support (Garisto et al., 2009a). Current safety assessments pessimistically assume several of the containers

will be emplaced with undetected defects, and then assess the impacts (Garisto et al., 2004).

The clay material in contact with the container is referred to as the “buffer” and is composed of compacted bentonite. This material swells as it saturates with water to fill any spaces or gaps, and so provides a tight, low permeability layer around the container. Beyond the buffer, the vault is filled with backfill, a 5:25:70 mix of bentonite, clay and granite aggregate. Surrounding the vault, are two regions of variably fractured rock, formed during the vault excavation process, and known as the excavation damaged zone (EDZ).

In this work, a COMSOL model was built which includes a dose dependent used fuel dissolution rate. The releases of radionuclides through a pin-hole defect in the container and their subsequent transport through the vault are modeled.

The vault portion of the COMSOL model was used to verify the radionuclide releases calculated by SYVAC-CC4, a safety assessment code developed by the NWMO. The near field model in SYVAC-CC4 is a simplified representation of the engineered barrier system. A series of concentric cylinders of varying thicknesses is used to approximate transport through the buffer backfill and EDZ.

By developing a more robust representation of the vault in COMSOL, processes such as time dependent defect size, corrosion, advective flow, and multiple nearby defective containers can be examined in more detail.

2. Model Description and Assumptions

In the COMSOL model, the container is emplaced vertically in boreholes drilled into the emplacement room floor and surrounded by buffer (Figure 1). The copper container is represented as a void in order to ensure no-flux boundary conditions at the container walls. The inside of the container is connected to the buffer by a pin-hole defect in the container.

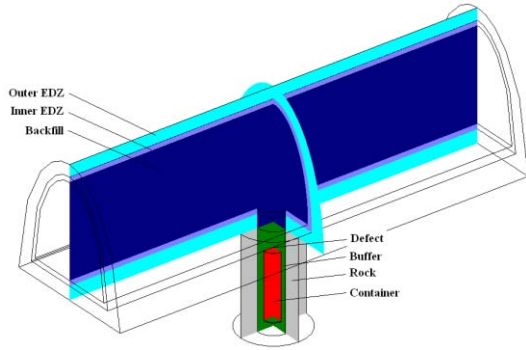


Figure 1: Model domain illustrating the orientation of the container, buffer, backfill, rock and damage zones (Note the pin-hole is so small that it is not visible in this figure. See Figure 5 for a better view of the defect)

The COMSOL model calculates the release of radionuclides by simulating the dissolution of the uranium fuel matrix and subsequent releases through the pin-hole defect in the container. Three radionuclides are considered in the model, Ca-41, Cs-135 and I-129. These radionuclides were chosen because of their importance in previous safety assessments and their range of sorption coefficients.

Several assumptions have been made in the development of the model. The model assumes:

- Water enters the container after the buffer saturates with water. This is assumed to occur 100 years from the start of repository operation. This will correspond to a model time of zero;
- The model environment is reducing, transport is diffusion dominated and all materials are fully saturated at the start of the simulation; and
- The steel canister insert and fuel cladding are not considered transport barriers and are not included in the model.

3. Governing Equations

The governing equation for this diffusion dominated system is given by (1):

$$\theta_s \frac{\partial C_i}{\partial t} + \rho_b \frac{\partial C_{pi}}{\partial C_i} \frac{dC_i}{dt} + \nabla \cdot [-\theta_s \tau D_o \nabla C_i] = R_{Li} + R_{Pi} + S_{ci} \quad (1)$$

In the equation, C_i and C_{pi} denote the concentration of species i in the liquid and sorbed to the solid particles respectively; θ_s is the porosity; τ is the tortuosity of the media; and D_o is the free water diffusivity. R_{Li} and R_{Pi} describe reactions occurring in the liquid and in the solid while S_{ci} describes the solute source (see Section 3.1).

Radioactive decay is the only reaction considered in the model. It occurs throughout the model, in both the liquid (R_{Li}) and solid (R_{Pi}) phases and is described by (2 a) and (2 b) respectively.

$$R_{Li} = -\theta_s \frac{\ln(2)}{t_{1/2}^i} \cdot C_i \left[\frac{mol}{a} \right] \quad (2 a)$$

$$R_{Pi} = \rho_b \cdot \kappa_p \frac{\ln(2)}{t_{1/2}^i} \cdot C_i \left[\frac{mol}{a} \right] \quad (2 b)$$

In the above equations, $t_{1/2}^i$ is the half-life of the species i ; ρ_b is the bulk density of the solid; and κ_p is the linear sorption coefficient.

3.1 Solute Source Term

Two processes, which operate on very different time scales, control the rate of radionuclide releases from the fuel. First, radionuclides in the fuel cladding gap and in the grain boundaries are released rapidly after water contacts the fuel. This is referred to as the instant release fraction.

Second radionuclides in the fuel matrix are released as the fuel dissolves. Since ~95% of radionuclides are trapped within the fuel matrix, release of most radionuclides is controlled by fuel dissolution (Shoesmith, 2000).

Under reducing conditions, the chemical dissolution of uranium dioxide would be very slow. However, radiolysis of groundwater caused by α -, β - and γ - radiation will form oxidizing species (i.e., H_2O_2 and $OH\bullet$) which will promote fuel dissolution. The rate at which these oxidizing species are formed will vary with the type and strength of radiation. In this model, the rate of fuel dissolution attributed to α -, β - and γ - radiation is given by (3 a) – (3 c) respectively. The chemical dissolution rate of the fuel, independent of radiolysis, is given by (3 d). The sum of these equations yields the total fuel dissolution rate described by (3 e) (Gierszewski et al., 2004).

$$R_{\alpha} = A_{fuel} \cdot G_{\alpha} \cdot D_{\alpha}(t) \quad (3 \text{ a})$$

$$R_{\beta} = A_{fuel} \cdot G_{\beta} \cdot D_{\beta}(t) \quad (3 \text{ b})$$

$$R_{\gamma} = A_{fuel} \cdot G_{\gamma} \cdot D_{\gamma}(t) \quad (3 \text{ c})$$

$$R_{diss} = A_{fuel} \cdot R_{UChem} \quad (3 \text{ d})$$

$$R_{UO_2} = R_{\alpha} + R_{\beta} + R_{\gamma} + R_{diss} \quad (3 \text{ e})$$

Here, A_{fuel} is the effective surface area of the dissolving fuel; G_{α} , G_{β} and G_{γ} are empirical rate constants; R_{UChem} is the chemical dissolution rate independent of radiolysis; and $D_{\alpha}(t)$, $D_{\beta}(t)$ and $D_{\gamma}(t)$ are the time dependent alpha, beta and gamma dose rates respectively. The time dependent dose rates are based on the log-linear fit of the data presented in Garisto et al. (2009b).

Given the rate of fuel dissolution, the release rate of radionuclide i into the groundwater is calculated by (4) (Gierszewski et al, 2004).

$$R_i(t) = \frac{(1 - f_{IR}^i) I_{UO_2}^i(t)}{I_{o,UO_2}} R_{UO_2}(t) \left[\frac{mol}{a} \right] \quad (4)$$

where f_{IR}^i is the instant release fraction; $I_{UO_2}^i(t)$ is the inventory of radionuclide i at time t in UO_2 in the container, described by (5); I_{o,UO_2} is the initial inventory of UO_2 in the container; and R_{UO_2} is the UO_2 matrix degradation rate at time t described by (3 e).

Radioactive decay will cause the radionuclide inventory to change over time. To account for this, the inventory of radionuclides is calculated as follows (5)

$$I_{UO_2}^i(t) = I_{o,UO_2}^i \cdot e^{(-\ln(2)/t_{1/2}^i \cdot t)} \cdot m_u [mol] \quad (5)$$

In this equation, I_{o,UO_2}^i is the initial mass of radionuclide i per mass of uranium; and m_u is the mass of uranium in the container.

Therefore, the radionuclide source term in the container is defined by (6),

$$S_{ci} = \frac{R_i(t)}{V_{container}} \left[\frac{mol}{m^3 a} \right] \quad (6)$$

where, $V_{container}$ is the total volume of the container.

4. Initial and Boundary Conditions

The instant release fraction serves as an initial condition for the concentration of radionuclide in the container, described by (7).

$$C_{oi} = \frac{f_{IR}^i \cdot I_{UO_2}^i(t_f)}{V_{void}} \left[\frac{mol}{m^3} \right] \quad (7)$$

In the above equation, $I_{UO_2}^i(t_f)$ is the inventory of radionuclide i in the container at the time of container failure (t_f) (calculated using Equation (5)); and V_{void} is the void volume in the container (the total volume of the container minus the volume of the fuel).

In all other subdomains, the initial concentration of radionuclides is zero.

The model's boundary conditions are listed in Table 1 and applied to all species.

Table 1: Boundary conditions used in the model where, D_i is the effective diffusivity of specie i ; $C_{i,m}$ is the concentration of specie i in medium m ; n is the normal vector at the boundary; $N_{i,m}$ is the flux of specie i in medium m .

Boundary condition	Boundary name
No Flux $N_i = D_i \nabla C_i = 0$	Inner container walls Outer container walls Hole walls
Continuous $C_{i,1} = C_{i,2}$ $-n(N_{i,1} - N_{i,2}) = 0$	All internal boundaries
Constant concentration $C_i = 0$	Outer boundaries

5. Results

5.1 Development of a COMSOL Near-Field Model

The COMSOL model was built in stages of increasing complexity. The fuel dissolution and radionuclide release from the container portion was developed using two simplified geometries. The first consisted of a container and a pin-hole defect, while the second also included the buffer. A zero concentration boundary condition was applied at the exit of the pin-hole in the first model and to the outer buffer boundaries in the second model.

Three increasingly complex cases in terms of initial conditions and fuel dissolution were examined.

In the first case a constant concentration in the container equivalent to the concentration due to the instant release fraction was modeled (Section 5.1.2).

The second case considered instant release, and a constant fuel dissolution rate (Section 5.1.3).

Third, the releases due to instant release, dose dependent fuel dissolution and radioactive decay were examined (Section 5.1.4).

The releases calculated in the cases described above were compared to approximate analytical solutions. Analytically, the release rate from the container can be calculated using (8).

$$\text{Release rate} = \frac{C_{cont}}{R_{buffer} + R_{pinhole}} \quad (8)$$

where C_{cont} is the radionuclide concentration in the container, R_{buffer} is the resistance due to the buffer and $R_{pin-hole}$ is the resistance due to the pin-hole. The buffer and pin-hole resistances are defined in (9 a) and (9 b).

$$R_{buffer} = \frac{1}{4 \cdot r \cdot \tau \cdot \theta_s \cdot D_o} \quad (9 a)$$

$$R_{pinhole} = \frac{1}{\left(\frac{\pi \cdot r^2 \cdot D_o}{L}\right)} \quad (9 b)$$

where r is the radius of the pin-hole and L is the length of the pin-hole.

Once the fuel dissolution and radionuclide release portion was developed, the geometry was expanded to include the other vault components shown in Figure 1. The releases of I-129, Ca-41 and Cs-135 from the near field are presented and discussed below.

5.1.1 Measuring the flux from the container

COMSOL flux measurements at the pin-hole-buffer and pin-hole-container boundaries significantly underestimated the actual flux, despite refined meshing at these areas. The results obtained in this manner were inconsistent with mass balance, i.e., the flux out of the pin-hole was lower than the flux out of the buffer even at steady state.

This discrepancy was due to the small hole radius which caused important edge effects (Figure 5). As a solution, a cylindrical subdomain was built inside the defect to create a boundary where the flux was constant throughout the cross section (Figure 5). At this boundary, the flux out of the container could be accurately measured.

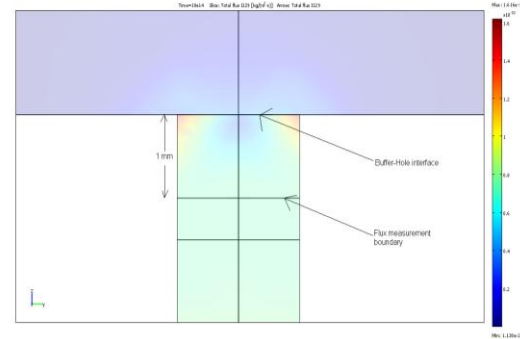


Figure 2: Slice plot showing the flux of I-129 near the buffer-hole interface. Areas in red indicate higher fluxes whereas areas in blue represent lower fluxes.

5.1.2 Radionuclide Release from a Container with a Constant Concentration

The purpose of this simulation was to validate the initial flux out of the container determined by COMSOL by comparing them to those calculated analytically (Table 2).

Table 2: Comparison of the flux out of the container when the concentration is constant in the container

	Flux [mol/a]	
	No buffer	With buffer
COMSOL	1.05×10^{-6}	1.95×10^{-7}
Analytical	1.13×10^{-6}	1.85×10^{-7}

The results obtained using COMSOL compare well to those calculated analytically. In the case without buffer, the flux calculated using COMSOL is slightly lower than that calculated analytically. This discrepancy is a result of the concentration gradient near the entrance of the pin-hole. The concentration at the entrance of the pin-hole is slightly lower than that of the container, thus the flux out of the container is slightly reduced in comparison to the analytical solution.

In the case with buffer, the flux calculated by COMSOL is slightly higher than the flux calculated analytically. This discrepancy may be due to the fact that the analytical solution is applicable to a semi-infinite geometry whereas the COMSOL model uses a $C = 0$ boundary condition at the boundaries of the (finite) model domain. Thus, concentration gradients and, hence, fluxes should be larger for the COMSOL model near the external boundaries of the model.

5.1.3 Radionuclide Release from a Container with a Constant Source Term

The results from this simulation are presented in Figure 3.

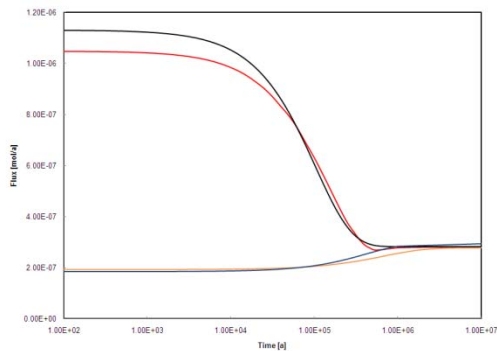


Figure 3: I-129 flux out of the container for a constant dissolution rate. Results for the case without buffer by COMSOL (red line) and analytic solution (black line) and for the case with buffer by COMSOL (orange line) and analytic solution (blue line) are shown.

As can be seen in Figure 3, the COMSOL and analytical solutions match very closely. At first, the fluxes are due to the initial concentration in the container and are equivalent to those presented in Table 2. With time, the system reaches steady state and the fluxes are equivalent to the rate of I-129 release from the fuel matrix.

5.1.4 Radionuclide Release from a Container with a Dose Dependent Source Term

In this simulation only the geometry which includes the buffer was considered. The COMSOL model results are compared to the analytical results in Figure 4. These solutions agree very closely. Both reach a peak concentration at approximately $\sim 10^5$ a. The peak flux calculated by COMSOL is slightly lower

than that determined analytically. However, at times beyond $\sim 2 \times 10^5$ a. the flux calculated by COMSOL is slightly higher than that calculated analytically.

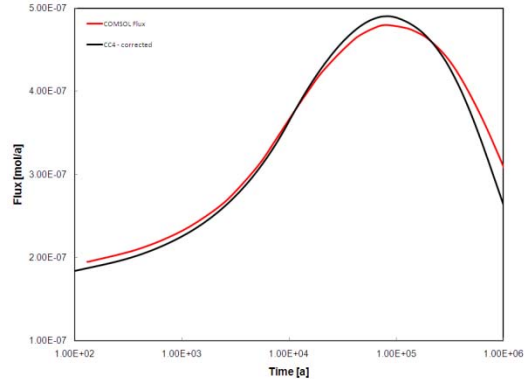


Figure 4: I-129 flux out of the container in a model with a dose dependent fuel dissolution rate calculated by COMSOL (red line) and analytically (black line)

5.1.5 Radionuclide Release from the Near Field

In this case, the entire vault geometry, as shown in Figure 1, was considered (in the previous calculations, only model features within the borehole were considered). By calculating the radionuclide flux through the model's outer boundaries, the flux out of the vault and into the geosphere can be compared to the flux out of the container. The comparisons are shown in Figures 5 - 7 for the radionuclides of interest.

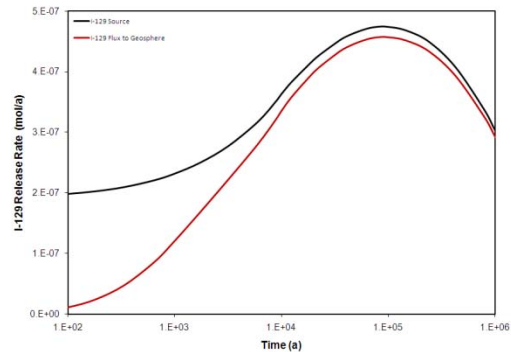


Figure 5: I-129 source out of container (black line) and release to geosphere (red line)

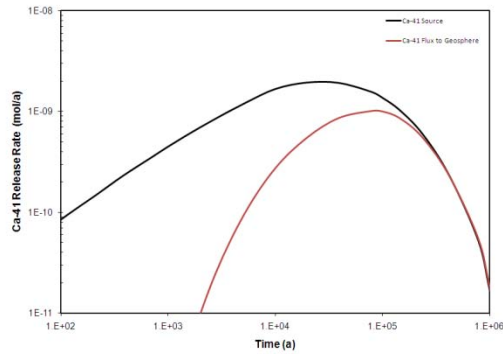


Figure 6: Ca-41 I-129 source out of container (black line) and release to geosphere (red line)

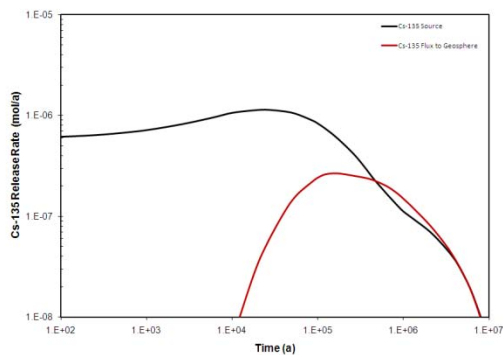


Figure 7: Cs-135 I-129 source out of container (black line) and release to geosphere (red line)

5.2 Verification of the SYVAC-CC4 Near Field Model

The near-field (or vault) portion of the SYVAC-CC4 safety assessment model is divided into two components: the container model in which the fuel dissolution rates and the radionuclide source term are calculated, and the vault model in which the transport through the engineered barrier system takes place.

In SYVAC-CC4 the engineered barrier system is represented by a series of concentric cylinders of a thicknesses specified by input data. By varying the thicknesses of the various vault materials the SYVAC-CC4 model can be used to mimic radionuclide releases from a vertically emplaced container.

In the verification of the SYVAC-CC4 vault model, the source term, i.e., the radionuclide release rate out of the container, as calculated by SYVAC-CC4 is directly used as input to the COMSOL model. Specifically, in the COMSOL model, this source is represented by a point on

the external boundary forming the top of the container.

The primary comparison between the two codes was the radionuclide flux from the vault into the geosphere, as shown in Figures 8-10.

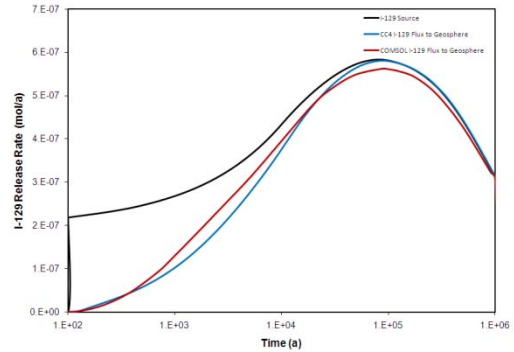


Figure 8: Comparison of I-129 releases into the geosphere: SYVAC-CC4 (blue) and COMSOL (red). The source is represented by the black line.

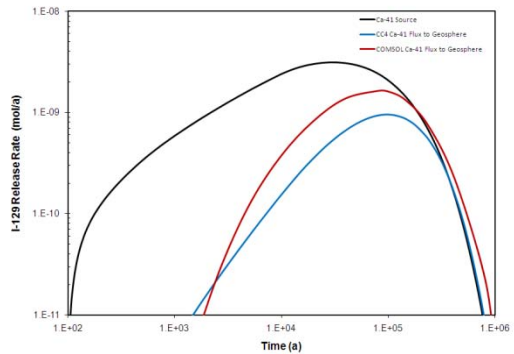


Figure 9: Comparison of Ca-41 releases into the geosphere: SYVAC-CC4 (blue) and COMSOL (red). The source is represented by the black line.

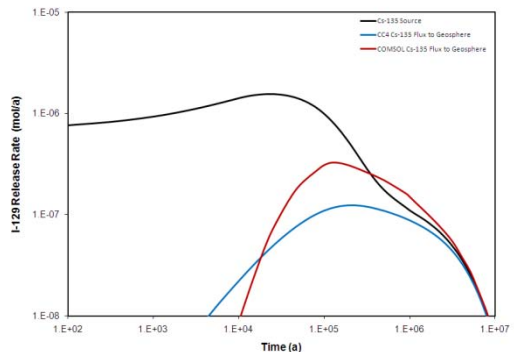


Figure 10: Comparison of Cs-135 releases into the geosphere: SYVAC-CC4 (blue) and COMSOL (red). The source is represented by the black line.

The differences in the two models are mainly due to the differences in the geometry. The SYVAC-CC4 model is limited in the amount of geometric detail that can be represented (since it was developed to model the horizontal borehole geometry) and cannot capture the complex path radionuclides actually take to exit the vault.

The primary radionuclides that contribute to long term doses are generally low or non-sorbing radionuclides (like I-129 and Cl-36). These radionuclides are very important in safety assessments. Thus, the buffer, backfill and EDZ layer thicknesses were selected so that the SYVAC-CC4 model would accurately calculate the releases into the geosphere for these nuclides for the vertical container geometry. The comparison in Figure 8 shows an excellent match between the SYVAC-CC4 and COMSOL models, indicating that the selected thicknesses are appropriate.

The match for higher sorbing radionuclides Ca-41 and Cs-135 is not as good in that COMSOL calculates higher releases than the SYVAC-CC4 model.

For the non-sorbing radionuclides the preferential path is up through the buffer and into the tunnel, necessitating a large buffer thickness in the SYVAC-CC4 model. Radionuclides with higher sorption coefficients have significantly increased transport resistance in the buffer and as a result will preferentially diffuse out the sides of the borehole and into the rock. This results in a shorter average path length and an underestimate of the releases by the SYVAC-CC4 model.

Generally, the two models were found to produce similar radionuclide flux curves with differences in the peak radionuclide fluxes of approximately 3%, 40% and 60% for I-129, Ca-41 and Cs-135 respectively.

6. Conclusions

A COMSOL model was built to calculate the releases of radionuclides from a defective used nuclear fuel container. The COMSOL model was developed in stages of increasing complexity. The agreement between the analytical and COMSOL I-129 releases from the container was very good. The releases of I-129, Ca-41 and Cs-135 from the entire vault were also calculated.

The COMSOL model was used to verify that SYVAC-CC4, a simplified safety assessment

code, can be used to accurately calculate radionuclide releases from a vertically emplaced container. It was found that for this geometry SYVAC-CC4 adequately models releases into the geosphere for I-129, the most important radionuclide from a safety perspective. However, for Ca-41 and Cs-135, which sorb strongly in the buffer, the peak radionuclide releases into the geosphere calculated by SYVAC-CC4 are lower than those calculated by COMSOL. This is likely because the buffer thickness used in the SYVAC-CC4 model was selected to ensure agreement between the SYVAC-CC4 and COMSOL models for non-sorbing radionuclides.

Future model developments could include processes such as time dependent defect size, corrosion, advective flow, multiple nearby defective containers and geosphere transport.

7. References

- Garisto, F., J. Avis, N. Calder, A. D'Adrea, P. Gierszewski, C. Kitson, T. Melnyk, K. Wei, L. Wojciechowski. *Third Case Study – Defective Container Scenario*. Ontario Power Generation, report: 06219-REP-01200-10126-R00, (2004)
- Garisto, F., T. Kempe and P. Gierszewski. *Technical Summary of the Safety Aspects of the Deep Geological Repository Concept for Used Nuclear Fuel*. Nuclear Waste Management Organization, report: NWMO TR-2009-12, (2009 a.)
- Garisto, F., D.H. Barber, E. Chen, A. Inglot and C.A. Morrison. *Alpha, Beta and Gamma Dose Rates in Water in Contact with Used CANDU Fuel*. Nuclear Waste Management Organization, report: NWMO TR-2009-27, (2009 b.)
- Gierszewski, P., T.W. Melnyk, S.C. Sheppard and J. Tait. *SYVAC-CC4 Theory (Version CC4.05)*. Ontario Power Generation, report: 06819-REP-01300-10072-R00, (2004)
- Shoesmith, D.W., Review – Fuel corrosion processes under waste disposal conditions, *Journal of Nuclear Materials*, **282**, 1-31(2000)