May 3, 2012

MEMORANDUM TO: Christepher McKenney, Chief
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and Environmental Protection
Office of Federal and State Materials
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SUBJECT: DESCRIPTION OF NRC STAFF SIMPLE ANALYTICAL AVERAGE-K_d AND DUAL-K_d MODELS

Enclosed please find a description of the simple analytical average-K_d and dual-K_d models generated by the U.S. Nuclear Regulatory Commission (NRC) staff to assess the fractional release rate of Tc at the Saltstone Disposal Facility (SDF). The results of these analyses were used to support the NRC staff review of the U.S. Department of Energy (DOE) performance assessment for the SDF and the development of the NRC staff's 2012 Technical Evaluation Report.

Docket No.: PROJ0734

Enclosure: As stated

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DESCRIPTION OF U.S. NUCLEAR REGULATORY COMMISSION STAFF SIMPLE ANALYTICAL AVERAGE-K_d AND DUAL-K_d MODELS

The U.S. Nuclear Regulatory Commission (NRC) staff created simple average-K_d and dual-K_d models in Microsoft Excel spreadsheets to evaluate the annual fractional release rate of Tc from saltstone as the saltstone waste form fractures and is oxidized. The models do not evaluate the potential attenuation of the Tc that is released from the saltstone in the disposal unit concrete and the environment. These models were created to support the NRC staff review of the revised performance assessment for the Saltstone Disposal Facility at the Savannah River Site (NRC, 2012b). In particular, the NRC staff used these models to evaluate the average-K_d approach (referred to by the U.S. Department of Energy (DOE) as a "single porosity" model) that DOE used in Cases K, K1, and K2[1] (SRR-CWDA-2011-00044). An independent peer review of the NRC staff simple average-K_d and dual-K_d models was performed by an NRC staff member (NRC, 2012a).

The NRC staff used these simple spreadsheet models for the following purposes:

1. To compare predicted fractional release rates estimated using the average-K_d and dual-K_d models (referred to by DOE as "single porosity" and "dual porosity" models respectively) and to investigate a potential modeling artifact in the average-K_d approach, and

2. To perform sensitivity analyses on the effect of key parameters (i.e., the effects of flow assumptions, fracture spacing, fracture growth rate, reducing capacity, and K_d values for Tc in oxidizing and reducing saltstone) on the calculated fractional release rates of Tc using the dual-K_d model.

Key Model Assumptions

In general, the models were designed to allow flexibility in the parameter values analyzed. In the sensitivity analysis performed by the NRC staff (NRC, 2012b), the following assumptions were made.

- Oxidation is modeled as being caused by both (1) oxygen diffusion in from the fracture faces and (2) dissolved oxygen in infiltrating water.
- Infiltrating water was assumed to be fully saturated with oxygen and fractures were assumed to have a non-depleting source of oxygen.
- Flow rates through saltstone were assumed to be equal to either (1) the flow rates calculated in DOE's Case K PORFLOW model, or (2) the hydraulic conductivity of saltstone.
- In calculations using flow rates based on the hydraulic conductivity of the saltstone:
  - the initial saltstone hydraulic conductivity is equal to 1×10^{-8} cm/s or 1×10^{-7} cm/s;
  - the saltstone hydraulic conductivity at 10,000 years is equal to 1×10^{-7} cm/s; and
  - the saltstone hydraulic conductivity at 20,000 years is equal to 1×10^{-6} cm/s.

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[1] DOE provided the NRC three cases related to Case K: Case K, Case K1, and Case K2. The only differences between these three cases are the K_d values used to represent Tc sorption in oxidizing and reducing cementitious materials (saltstone and disposal unit concrete). When this distinction is not important, the NRC staff uses the term "Case K" to refer to all three cases. The NRC staff differentiates between Cases K, K1, and K2 when discussing values specific to Tc (e.g., Tc Kd values).

- Fracture growth is assumed to occur either as a logarithmic or quadratic function of time.
- Initial fracture spacing is equal to 61 m (based on the width of Vault 4).
- Final fracture spacing is equal to either 0.1 m (DOE Case K value) or 1 m.
- Saltstone was assumed to be entirely reducing at the time of closure.
- Reducing capacity is equal to either 0.206 meq e^-/g (DOE Case K value) or 0.822 meq e^-/g (DOE Case A value).
- Oxidized Tc K_d is equal to 0.8 mL/g (DOE Case A and DOE Case K1 value).
- Reduced Tc K_d is equal to either 139 mL/g (based on SRNL-STI-2010-00667) or 500 mL/g (DOE Case K1 value).
- Diffusion between the oxidized and reduced regions was not included in the dual-K_d model.

Average-Kd Fractional Release Rate Calculations

In the average-K_d calculations, the fractional release rates of Tc are estimated using a weighted average sorption coefficient (K_d) value that is based on the fraction of saltstone oxidized. The weighted average K_d is calculated for each time step as shown in Equation (1). This approach is identical to the approach used by DOE in Case K (Eq. 11 in SRR-CWDA-2011-00044).

$$K_d = x_{Ox} * K_{d,ox} + x_{Re} * K_{d,Re} \qquad \text{(Equation 1)}$$

where:

x_{Ox}, x_{Re} = fraction of the saltstone that is oxidized or reduced during the given time step;

$K_{d,ox}$ = oxidized Tc K_d (assumed 0.8 mL/g consistent with DOE Case A and Case K1 value); and

$K_{d,Re}$ = reduced Tc K_d (assumed either 139 mL/g [based on SRNL-STI-2010-00667] or 500 mL/g [DOE Case K1 value]).

The concentration of Tc in the solid phase of the saltstone is adjusted for changes in the K_d value over time as the saltstone becomes more oxidized and less sorptive.

$$C_s = \frac{C_N}{(\rho_b + \frac{n}{K_d})} \qquad \text{(Equation 2)}$$

where:

C_s = concentration of Tc in the saltstone solid corrected for the K_d during the given time step (g Tc/g saltstone solid);

C_N = normalized concentration of saltstone (g Tc/cm^3 saltstone) (includes Tc in the solid + aqueous phases);

ρ_b = bulk density of the solid (1.01 g/mL); and

n = porosity (0.58 unitless).

The annual fractional release rate of Tc is then calculated using Equation 3. Modeled releases are stopped when the Tc in saltstone is depleted.

$$FRR = \frac{Q*C_s}{K_d} \qquad \text{(Equation 3)}$$

where:

FRR = annual fractional release rate (1/yr); and

Q = flow through saltstone matrix (L/yr)
(see below for details on flow rate assumptions).

Dual-K_d Fractional Release Rate Calculations

In the dual-K_d model, the releases of Tc from the oxidized and reduced regions are calculated separately. In this model, the amount of Tc that is in the oxidized form is calculated for each time step based on the amount initially present plus the additional oxidation that occurs during the time step minus the Tc released during the time step. The concentrations of Tc in the saltstone solid in the oxidized and reduced regions are partitioned between solid and aqueous phase with the K_d in the same way as they are in the average-K_d model (Equation 2). However, because in the dual-K_d model the K_d values in oxidized and reduced saltstone remain constant with time, the concentration of Tc in any particular region of the saltstone solid also is constant until that region changes from a reduced state to an oxidized state.

The annual fractional release rate of Tc from the oxidized region is calculated using Equation 4 unless the Tc in the oxidized form is depleted. To determine if the Tc inventory in the oxidized region is depleted, the cumulative release from the oxidized region is tracked, as are additions to the inventory of the oxidized region as more saltstone is oxidized. If the calculated release from the oxidized region exceeds the amount of Tc remaining in the oxidized region, the release is limited by the total amount of Tc in the oxidized form.

$$FRR_{ox} = \frac{Tot_{ox} *Q* C_{s,ox}}{K_{d,ox}} \qquad \text{(Equation 4)}$$

where:

FRR_{ox} = annual fractional release rate from oxidized saltstone (1/yr);

Tot_{ox} = total fraction of Tc that is in the oxidized form;

Q = flow through saltstone matrix (L/yr) (see below for details on; flow rate assumptions)

$C_{s,ox}$ = concentration of Tc partitioned onto the saltstone solid based on the oxidized Tc K_d (g Tc/g saltstone solid); and

$K_{d,ox}$ = oxidized Tc K_d (assumed 0.8 mL/g consistent with DOE Case A and Case K1 value).

$$FRR_{red} = \frac{(1 - Tot_{ox}) * Q * C_{s,red}}{K_{d,red}}$$ (Equation 5)

where:

FRR_{red} = annual fractional release rate from reduced saltstone (1/yr);

$C_{s,red}$ = concentration of Tc partitioned onto the saltstone solid based on the reduced Tc K_d (g Tc/g saltstone solid); and

$K_{d,red}$ = reduced Tc K_d (assumed either 139 mL/g [based on SRNL-STI-2010-00667] or 500 mL/g [DOE Case K1 value]).

The total fractional release was calculated by summing the release from the oxidized and reduced regions until the Tc in the saltstone is depleted.

$$FRR = FRR_{ox} + FRR_{red}$$ (Equation 6)

Flow Rates

The model allows the user to select the flow rate of infiltrating water through the saltstone based on (1) a constant rate, (2) the flow rates calculated by DOE in the Case K PORFLOW model (NRC, 2010) or (3) user-defined values of the hydraulic conductivity of the saltstone. Because the model always limits the flow based on the selected hydraulic conductivity, to use the option of setting the flow equal to the DOE Case K flow rate, the user must ensure that the selected hydraulic conductivity values are not limiting (i.e., by setting them to high values). Similarly, because the model always limits the flow by the constant flow rate specified, the user must ensure the value specified for the constant flow rate is large enough to not limit flow when the user is analyzing flow rates based on PORFLOW or the hydraulic conductivity. The model is constructed in this manner to allow an external limit on the maximum flow to be imposed (e.g., the maximum infiltration through the cap or natural infiltration rate). For the calculations used to support the staff’s SDF TER (NRC, 2012b), the staff performed model runs based on the DOE Case K flow rate and model runs based on the saltstone hydraulic conductivity. For the evaluations that used a flow rate determined from assumed hydraulic conductivity values for the saltstone, the hydraulic conductivity at the time of closure was assumed to be either 1×10^{-7} cm/s or 1×10^{-8} cm/s. The hydraulic conductivity was assumed to be 1×10^{-7} cm/s at 10,000 years following closure and 1×10^{-6} cm/s at 20,000 years following closure. In the calculations in which the initial hydraulic conductivity was assumed to be 1×10^{-8} cm/s, the hydraulic conductivity was assumed to increase linearly to 1×10^{-7} cm/s over the first 10,000 years. In the calculations in which the initial hydraulic conductivity was assumed to be 1×10^{-7} cm/s, the hydraulic conductivity was assumed to remain constant for the first 10,000 years. In all cases, the hydraulic conductivity was assumed to increase linearly to 1×10^{-6} cm/s at 20,000 years.

Calculation of Fracture Spacing

The fracture spacing is assumed to occur either as a logarithmic or quadratic function of time. The initial fracture spacing, or block width, is assumed to be 61 m (i.e., the width of Vault 4. The maximum number of fractures is assumed to occur at 10,000 years and the maximum fracture spacing is assumed to be either 0.1 m (i.e., the value assumed by DOE in Case K) or 1 m. No further degradation is assumed to occur after 10,000 years and the fracture spacing is assumed to remain constant.

Fracture growth as a logarithmic function of time

The calculation of fracture growth as a logarithmic function of time is based on the approach DOE used for Case K (i.e., based on Eq. 3 in SRR-CWDA-2011-00044). For the first 10,000 years of the analysis, the fracture spacing (i.e., the block width) is estimated using Equation 7.

$$\log(B) = \frac{(\log(B_{max}) - \log(B_i))*t}{t_{max}} + \log(B_i) \qquad \text{(Equation 7)}$$

where:

B = fracture spacing at time t (m);

B_{max} = minimum fracture spacing (assumed either 0.1 m [DOE Case K value] or 1 m);

B_i = initial fracture spacing (61 m);

t = time (years); and

t_{max} = time minimum fracture spacing occurs (assumed 10,000 years, consistent with DOE Case K).

The number of exposure faces was then calculated from the fracture spacing using Equation 8.

$$N = 2* \frac{W}{B} \qquad \text{(Equation 8)}$$

where:

N = number of exposure faces at time t; and

W = width of the disposal unit (61 m).

Fracture growth as a quadratic function of time

To investigate the potential fractional release rates when a less sudden rate of fracture formation is assumed, the fractional release rates were also calculated assuming the fracture growth occurred as a quadratic function of time. In these calculations, the number of exposure faces as a function of time was estimated using Equation 9.

$$N = 2 * \left(\frac{\text{fractures}_{max} * t^2}{t_{max}^2} + \text{fractures}_{init}\right) \qquad \text{(Equation 9)}$$

where:

N = number of exposure faces at time t;

fractures_{init} = initial number of fractures (1 fracture);

fractures_{max} = maximum number of fractures (610 fractures [a fracture every 0.1 m] or 61 fractures [a fracture every 1 m]);

t = time (years); and

tmax = time at which maximum number of fractures is reached (10,000 years).

Calculation of Amount of Saltstone Oxidized

In the NRC calculations, the oxidation of the saltstone was assumed to occur due to both diffusion of oxygen into the saltstone matrix from fracture faces and from infiltrating water advectively transporting oxygen into the saltstone. This differs from the Case K calculations performed by DOE which only included oxidation from the diffusion of oxygen from fractures. As was assumed by DOE in Case K, the calculation of the fraction of saltstone oxidized included the conservative assumption that the concentration of oxygen in water in the fractures and in the infiltrating water was equal to its saturated value (1.06 meq e^-/L). The NRC calculations also used the same parameter values as DOE used in Case K for the porosity, effective diffusion coefficient, and bulk density of the saltstone.

The NRC staff models used the same approach as DOE used in the Case K model (Eq. 14 in SRR-CWDA-2011-00044) to determine the amount of oxidation due to the diffusion of oxygen from fracture faces. This approach was based on the methodology described in Smith and Walton (1993).

$$\delta(t) = \left[\frac{2nD_e c_{ox}}{r_{ox}\rho_b} t\right]^{1/2} \qquad \text{(Equation 10)}$$

where:

$\delta(t)$ = depth of oxidation from fracture face at time t;

n = porosity (0.58);

D_e = effective diffusion coefficient (1×10^{-7} cm^2/s);

c_{ox} = dissolved oxygen concentration at the fracture face (1.06 meq e-/L);

r_{ox} = reduction capacity of the solid (0.206 meq e^-/g [DOE Case K value] or 0.822 meq e^-/g [DOE Case A value]);

ρ_b = bulk density of the solid (1.01 g/mL); and

t = time (years).

The cumulative oxidation thickness was then calculated using the same method as DOE used in Case K (Eq. 15 in SRR-CWDA-2011-00044 and Equation 11 below):

$$\delta_T = N_1 * \delta(t-\tau_1) + (N_2-N_1) * (t-\tau_2) + (N_3-N_2) * \delta(t-\tau_3)+\ldots \quad \text{(Equation 11)}$$

where:

N_i = number of exposure faces at time τ_i.

The total fraction of the saltstone monolith that is oxidized due to the diffusion of oxygen at a given time step was then calculated using Equation 12.

$$x_{ox,\ diff} = \frac{\delta_T}{W} \quad \text{(Equation 12)}$$

where:

$x_{ox,diff}$ = fraction of the wasteform that is oxidized due to diffusion of oxygen from the fracture faces; and

W = width of the disposal unit (61 m).

The fraction of the saltstone that is oxidized by oxygen in infiltrating water during the time step was calculated using Equation 13.

$$ox_{adv} = \frac{Q * c_{ox} * TS}{r_{ox}} \quad \text{(Equation 13)}$$

where:

ox_{adv} = fraction of saltstone oxidized during the time step due to oxygen advectively transported into saltstone;

Q = flow through saltstone matrix (L/yr) (see above for details on flow rate assumptions);

c_{ox} = dissolved oxygen concentration at the fracture face (1.06 meq e-/L);

r_{ox} = reduction capacity of the solid (0.206 meq e^-/g [DOE Case K value] or 0.822 meq e^-/g [DOE Case A value]); and

TS = length of time step (years).

The total cumulative fraction of saltstone oxidized due to oxygen in infiltrating water ($x_{ox,adv}$) was then determined by summing the fraction oxidized during the current and previous time steps.

The total fraction of the saltstone that is oxidized at the given time step was then determined by summing the fraction of the saltstone oxidized through diffusion of oxygen and the fraction of the saltstone oxidized through infiltration of oxygen containing water, except that a check was performed so that areas that would be oxidized by both processes were not double counted. If this sum was found to be greater than one, the total fraction oxidized was set to a value of one.

$$x_{ox} = \min\ [x_{ox,diff} + x_{ox,adv},\ 1] \quad \text{(Equation 14)}$$

References

Smith R.W. and J.C. Walton, *The role of Oxygen Diffusion in the Release of Technetium from Reducing Cementitious Waste Forms*. Materials Research Society Symposium Proceedings, Vol 294. 1993.

SRNL-STI-2010-00667 Rev 0, Almond, P.M., and Kaplan, D.I., *Distribution Coefficients (Kd) Generated from a Core Sample Collected from the Saltstone Disposal Facility*. Savannah River National Laboratory. Aiken, SC. April 30, 2011. ML113320284.

SRR-CWDA-2009-00017, SRR, *Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site*. Savannah River Site. Aiken, SC. October 29, 2009. ML101590008.

SRR-CWDA-2011-00044 Rev. 0, SRR, *Comment Response Matrix for NRC - Second Request for Additional Information on the Saltstone Disposal Facility Performance Assessment*. SRR. Aiken, SC. April 21, 2011. ML111180141.

U.S. Nuclear Regulatory Commission (NRC), *Index for Saltstone Performance Assessment PORFLOW™ and GoldSim® Model Files Provided by DOE in 2010*. NRC. Washington, DC. November 2, 2010. ML103060015.

U.S. Nuclear Regulatory Commission (NRC), *Review of Staff Release Rate Calculations for Saltstone*. NRC. Washington, DC. April 2, 2012a. ML120880224.

U.S. Nuclear Regulatory Commission (NRC), *Technical Evaluation Report for the Revised Performance Assessment for the Saltstone Disposal Facility at the Savannah River Site, South Carolina*. NRC. Washington, DC. April 30, 2012b. ML121170309.