



SRNL-L4321-2011-00004

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Subject: **Oxidation of Fractured Cementitious Materials in Performance Assessments**

Performance Assessment (PA) modeling for the groundwater pathway is typically focused on liquid phase transport processes in the vadose and aquifer zones. However, gas phase transport of oxygen through fractures is a controlling process for slag and Tc-99 oxidation in reducing grouts and concretes under unsaturated conditions. Simulation of combined gas and liquid phase transport is not supported by currently available versions of PORFLOW to our knowledge, and explicit representation of fractures is not feasible except for special cases involving a relatively small number of fractures. To overcome these limitations, the analytical approach of Smith and Walton (1993) can be used to predict transient oxidation external to PORFLOW. The results of this analysis can be transformed into an effective Tc-99 sorption coefficient reflecting varying oxidation through time. The derived sorption coefficient can then be used in a conventional liquid phase only PORFLOW simulation, thus implicitly accounting for both gas and liquid phase oxygen transport in fractured cementitious materials.

Concept

Oxidation is assumed to occur as multiple one-dimensional moving fronts across the reducing material, emanating from multiple exposure faces. For simplicity, one is depicted in Figure 1.

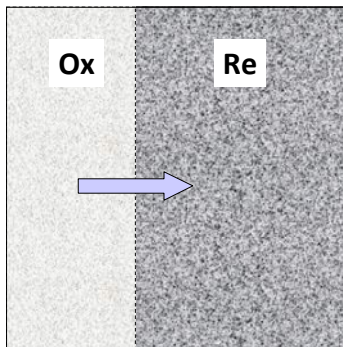


Figure 1 - Partially oxidized cementitious material.

Composite sorption coefficient

Let the fractions of oxidized and reduced material be denoted by x_{Ox} and x_{Re} such that

$$x_{Ox} + x_{Re} = 1 \quad (1)$$

The total mass of a species in a porous medium with sorption is

$$M = Vnc + V(1-n)\rho_s c_s \quad (2)$$

where V = volume, n = porosity, ρ_s = solid density, c = liquid concentration, and c_s = solid concentration. For linear sorption

$$c_s = K_d c \quad (3)$$

where K_d = sorption coefficient, and Equation (2) becomes

$$\begin{aligned} M &= Vnc + V(1-n)\rho_s K_d c \\ &= Vnc \left[1 + \frac{(1-n)\rho_s K_d}{n} \right] \\ &= VncR \end{aligned} \quad (4)$$

The retardation factor R is defined by

$$R = 1 + \frac{(1-n)\rho_s K_d}{n} \quad (5)$$

The total species mass in the oxidized and reduced regions is

$$VncR = x_{Ox} VncR_{Ox} + x_{Re} VncR_{Re} \quad (6)$$

where the liquid concentration has been assumed to be in equilibrium between the oxidized and reduced regions and R is the effective retardation for the composite of oxidized and reduced material. Equation (6) simplifies to

$$R = x_{Ox} R_{Ox} + x_{Re} R_{Re} \quad (7)$$

The composite sorption coefficient is derived as

$$R - 1 = x_{Ox} R_{Ox} + x_{Re} R_{Re} - (x_{Ox} + x_{Re})$$

$$\frac{(1-n)\rho_s K_d}{n} = x_{Ox} \frac{(1-n)\rho_s K_{d,Ox}}{n} + x_{Re} \frac{(1-n)\rho_s K_{d,Re}}{n}$$

$$K_d = x_{Ox} K_{d,Ox} + x_{Re} K_{d,Re} \quad (8)$$

Fracture spacing

For hydraulic property specification, degradation of cementitious materials is assumed to take the form of one-dimensional fractures at a spacing B that varies through time according to the relationship (SRNL-L6200-2010-00026, Rev. 1)

$$\log_{10}(B) = \begin{cases} \infty & t \leq t_{0\%} \\ \frac{\log_{10}(B_{100\%}) - \log_{10}(B_{0\%})}{\log_{10}(t_{100\%}) - \log_{10}(t_{0\%})} [\log_{10}(t) - \log_{10}(t_{0\%})] + \log_{10}(B_{0\%}) & t_{0\%} < t < t_{100\%} \\ \log_{10}(B_{100\%}) & t \geq t_{100\%} \end{cases} \quad (9)$$

where t is elapsed time and the subscripts refer to 0% and 100% degradation. The evaluation time is defined as the midpoint of the flow simulation period in log-space, i.e.,

$$\log_{10}(t) = 0.5[\log_{10}(t_{TI-}) + \log_{10}(t_{TI+})] \quad (10)$$

where t_{TI-} and t_{TI+} are the start and end times of the flow time interval (TI). For a material zone of dimension W transverse to cracking (width), the number of exposure faces is

$$N = 2 \frac{W}{B} \quad (11)$$

counting the left and right boundaries. Note that each fracture creates two exposure faces. Equation (11) can be generalized to handle large B (greater than W) as

$$N = \max \left[2 \frac{W}{B}, N_{\min} \right] \quad (12)$$

where N_{\min} is the minimum number of exposure faces. In practice one would choose 0 (infinite medium), 1 (semi-infinite medium), or 2 (finite medium).

Oxidation process

The intact matrix between exposure faces is assumed to have sufficiently low permeability that oxygen transport is by diffusion only within the matrix. Fractures are assumed to air-filled, except for thin liquid films on each exposure face, such that the concentration of dissolved oxygen is held constant at its

saturation value (1.06 meq e-/L) at each face. The oxidation process is then independent of the flow through fractures, i.e., the system flow model. The oxidation front advances at a rate defined by the differential equation (Smith and Walton, 1993)

$$r_{Ox}\rho_b \frac{d\delta}{dt} = \frac{nD_e c_{Ox}}{\delta} \quad (13)$$

where r_{Ox} = reduction capacity of solid [meq e-/g], ρ_b = bulk density of solid [g/mL], δ = position of oxidation front from the exposure face [cm], t = elapsed time [s], n = porosity [-], D_e = effective diffusion coefficient [cm^2/s], and c_{Ox} = dissolved oxygen concentration at the exposure face [meq e-/mL]. The analytic solution to Equation (13) is

$$\delta(t) = \left[\frac{2nD_e c_{Ox}}{r_{Ox}\rho_b} t \right]^{1/2} \quad (14)$$

For exposure faces created at different discrete times, the cumulative oxidation thickness is the convolution

$$\delta_T = N_1 \cdot \delta(t - \tau_1) + (N_2 - N_1) \cdot \delta(t - \tau_2) + (N_3 - N_2) \cdot \delta(t - \tau_3) + \dots \quad (15)$$

where N_i = total exposure faces through time τ_i . Equation (15) assumes that each new fracture exposes fresh material and each oxidation front advances independent of others. The fraction of material oxidized becomes

$$x_{Ox} = \min \left[\frac{\delta_T}{W}, 1 \right] \quad (16)$$

The effective sorption coefficient can then be computed from Equation (8).

Example calculation

As an example application, consider a 60 meter wide grout monolith with the material properties of saltstone. For this hypothetical example, the grout is not contained within a concrete vault. Input specifications are listed in Table 1. For a selected sequence of time periods, analysis results are provided in Table 2. The indicated sorption coefficient is associated with the end of the time period. Figure 2 provides a plot of the transient blended sorption coefficient.

Table 1 - Input specifications

Parameter	Value
$t_{0\%}$ (yr)	10
$t_{100\%}$ (yr)	10000
$B_{0\%}$ (m)	10000
$B_{100\%}$ (m)	0.1
$K_{d, Ox}$ (mL/g)	1
$K_{d, Re}$ (mL/g)	1000
n (-)	0.58
D_e (cm ² /s)	1.00E-07
c_{Ox} (meq e-/mL)	0.00106
r_{Ox} (meq e-/g)	0.822
ρ_b (g/mL)	1.008
$\frac{2nD_e c_{Ox}}{r_{Ox} \rho_b}$ (cm ² /s)	1.48E-10
(m ² /yr)	4.68E-07
W (m)	60
N_{min} (-)	2

Table 2 - Effective sorption coefficient calculation.

TI	t _{Beg} (yr)	t _{End} (yr)	t _{Mid} (yr)	W	B	N	ΔN	δ _T	time (yr)	x _{Ox}	x _{Re}	K _d
TI01	0	50	7.1	60	10000.00	2.0	2.00	0.010	50	0.000	1.000	999.8
TI02	50	100	70.7	60	383.88	2.0	0.00	0.014	100	0.000	1.000	999.8
TI03	100	150	122.5	60	153.67	2.0	0.00	0.017	150	0.000	1.000	999.7
TI04	150	200	173.2	60	86.24	2.0	0.00	0.019	200	0.000	1.000	999.7
TI05	200	250	223.6	60	56.35	2.1	0.13	0.022	250	0.000	1.000	999.6
TI06	250	300	273.9	60	40.19	3.0	0.86	0.029	300	0.000	1.000	999.5
TI07	300	350	324.0	60	30.36	4.0	0.97	0.037	350	0.001	0.999	999.4
TI08	350	400	374.2	60	23.89	5.0	1.07	0.048	400	0.001	0.999	999.2
TI09	400	450	424.3	60	19.38	6.2	1.17	0.060	450	0.001	0.999	999.0
TI10	450	500	474.3	60	16.09	7.5	1.27	0.074	500	0.001	0.999	998.8
TI11	500	600	547.7	60	12.66	9.5	2.02	0.105	600	0.002	0.998	998.3
TI12	600	700	648.1	60	9.56	12.6	3.07	0.146	700	0.002	0.998	997.6
TI13	700	800	748.3	60	7.53	16.0	3.40	0.194	800	0.003	0.997	996.8
TI14	800	900	848.5	60	6.10	19.7	3.72	0.250	900	0.004	0.996	995.8
TI15	900	1000	948.7	60	5.07	23.7	4.02	0.315	1000	0.005	0.995	994.8
TI16	1000	1200	1095.4	60	3.99	30.1	6.42	0.456	1200	0.008	0.992	992.4
TI17	1200	1400	1296.1	60	3.01	39.8	9.74	0.640	1400	0.011	0.989	989.3
TI18	1400	1600	1496.7	60	2.37	50.6	10.79	0.858	1600	0.014	0.986	985.7
TI19	1600	1800	1697.1	60	1.92	62.4	11.79	1.112	1800	0.019	0.981	981.5
TI20	1800	2000	1897.4	60	1.60	75.2	12.76	1.401	2000	0.023	0.977	976.7
TI21	2000	2300	2144.8	60	1.30	92.2	17.04	1.881	2300	0.031	0.969	968.7
TI22	2300	2600	2445.4	60	1.05	114.8	22.54	2.462	2600	0.041	0.959	959.0
TI23	2600	2900	2745.9	60	0.86	139.2	24.45	3.128	2900	0.052	0.948	947.9
TI24	2900	3200	3046.3	60	0.73	165.5	26.30	3.882	3200	0.065	0.935	935.4
TI25	3200	3600	3394.1	60	0.61	198.2	32.68	4.991	3600	0.083	0.917	916.9
TI26	3600	4000	3794.7	60	0.50	238.7	40.50	6.286	4000	0.105	0.895	895.3
TI27	4000	4500	4242.6	60	0.42	287.5	48.78	8.093	4500	0.135	0.865	865.3
TI28	4500	5000	4743.4	60	0.35	346.2	58.75	10.190	5000	0.170	0.830	830.3
TI29	5000	5500	5244.0	60	0.29	409.2	63.02	12.560	5500	0.209	0.791	790.9
TI30	5500	6000	5744.6	60	0.25	476.4	67.15	15.200	6000	0.253	0.747	747.0
TI31	6000	6500	6245.0	60	0.22	547.5	71.15	18.100	6500	0.302	0.698	698.6
TI32	6500	7000	6745.4	60	0.19	622.6	75.05	21.290	7000	0.355	0.645	645.6
TI33	7000	7500	7245.7	60	0.17	701.4	78.85	24.750	7500	0.412	0.588	587.9
TI34	7500	8000	7746.0	60	0.15	784.0	82.56	28.490	8000	0.475	0.525	525.6
TI35	8000	8500	8246.2	60	0.14	870.2	86.19	32.520	8500	0.542	0.458	458.6
TI36	8500	9000	8746.4	60	0.13	959.9	89.74	36.830	9000	0.614	0.386	386.7
TI37	9000	9500	9246.6	60	0.11	1053.1	93.23	41.440	9500	0.691	0.309	310.0
TI38	9500	10000	9746.8	60	0.10	1149.8	96.65	46.340	10000	0.772	0.228	228.5
TI39	10000	11000	10488.1	60	0.10	1200.0	50.21	54.360	11000	0.906	0.094	94.9
TI40	11000	12000	11489.1	60	0.10	1200.0	0.00	60.660	12000	1.000	0.000	1.0
TI41	12000	15000	13416.4	60	0.10	1200.0	0.00	75.970	15000	1.000	0.000	1.0
TI42	15000	20000	17320.5	60	0.10	1200.0	0.00	95.840	20000	1.000	0.000	1.0
TI43	20000	50000	31622.8	60	0.10	1200.0	0.00	171.600	50000	1.000	0.000	1.0
TI44	50000	100000	70710.7	60	0.10	1200.0	0.00	251.300	100000	1.000	0.000	1.0

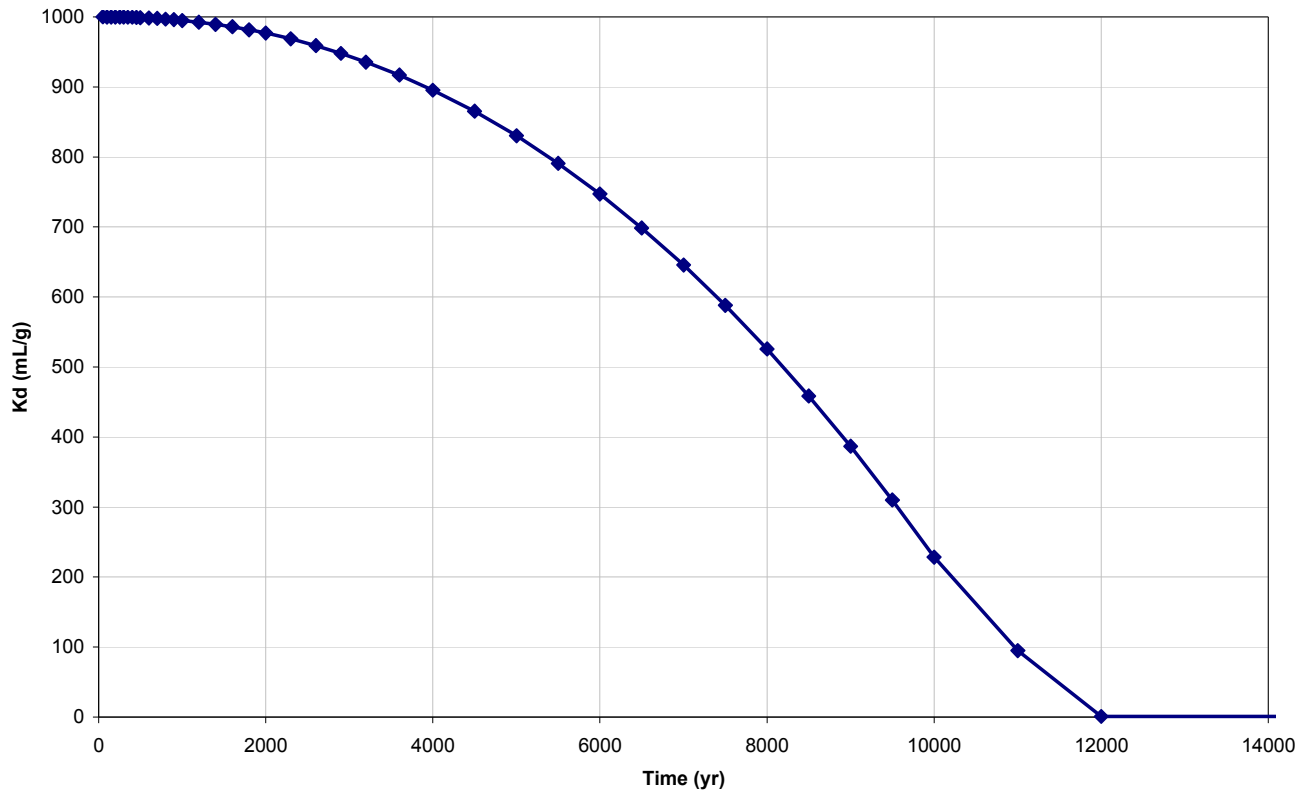


Figure 2 - Effective sorption coefficient for partially oxidized cementitious material.

References

Smith, R. W. and J. C. Walton. 1993. *The role of oxygen diffusion in the release of technetium from reducing cementitious waste forms*. Mat. Res. Soc. Symp. Proc. Vol. 294.

Appendix - PYTHON program

```
#!/usr/bin/env python

import sys
import math

#compute effective Kd for oxidizing cementitious material - - - - -
def effectiveKd(TI, tBeg, tEnd,\
  t_0, t_100, B_0, B_100,\
  Kd_Ox, Kd_Re, n, D_e, c_Ox, r_Ox, rho_b,\
  W, minN,\
  time, x_Ox, x_Re, Kd):

  paramGroup_cm2_s = (2*n*D_e*c_Ox)/(r_Ox*rho_b)
  #cm2/s parameter grouping in diffusion model
  paramGroup = paramGroup_cm2_s*(3600*24*365)/(100*100)
  #m2/yr preferred units going forward

  if (1):
    print ""
    print "---Parameter settings---"
    print "t_0 (yr): %g" % t_0
    print "t_100 (yr): %g" % t_100
    print "B_0 (m): %g" % B_0
    print "B_100 (m): %g" % B_100

    print "Kd_Ox (mL/g): %g" % Kd_Ox
    print "Kd_Re (mL/g): %g" % Kd_Re
    print "n (-): %g" % n
    print "D_e (cm2/s): %g" % D_e
    print "c_Ox (meq e-/mL): %g" % c_Ox
    print "r_Ox (meq e-/g): %g" % r_Ox
    print "rho_b (g/mL): %g" % rho_b
    print "paramGroup (cm2/s): %g" % paramGroup_cm2_s
    print " (m2/yr): %g" % paramGroup

    print "W (m): %g" % W
    print "minN (-): %g" % minN

    print ""
    print "TI\ttBeg (yr)\ttEnd (yr)\ttMid (yr)\tW\tB\tN\tdN\tdTotal\ttime
(yr)\tx_Ox\tx_Re\tKd"

  N = [0]
  dN = []
  dTotal = []
  for i in range(len(TI)):
    tMid = 10**(0.5*(math.log10(max(tBeg[i],1)) + math.log10(tEnd[i])))
    if (tMid <= t_0):
      B = B_0
    elif (tMid >= t_100):
      B = B_100
    else:
      slope = (math.log10(B_100) - math.log10(B_0))/ \
        (math.log10(t_100) - math.log10(t_0))
      log10B = slope*(math.log10(tMid) - math.log10(t_0)) + math.log10(B_0)
```



```

        B = 10**log10B          #m      fracture spacing

totalFractures = 2*(float(W)/float(B)) #-      total number of fracture faces
totalFractures = max(totalFractures,minN)
N.append(totalFractures)

addedFractures = N[i+1] - N[i] #-      added number of fracture faces
dN.append(addedFractures)

delta = 0
delTI = []
for j in range(i+1):          #sum oxidation from fractures created in each period
    delj = dN[j]*math.sqrt(paramGroup*(tEnd[i]-tBeg[j]))
    delta = delta + delj
    delTI.append(delj)
    if (0):
        print i,j,dN[j],tBeg[j],tEnd[i],delTI[j]
dTotal.append(delta)          #m      total oxidation thickness

time.append(tEnd[i])          #yr      time

oxidizedFraction = min(dTotal[i]/W,1)
x_Ox.append(oxidizedFraction) #-      fraction oxidized

reducedFraction = 1 - oxidizedFraction
x_Re.append(reducedFraction)  #-      fraction reduced

sorptionCoefficient = x_Ox[i]*Kd_Ox + x_Re[i]*Kd_Re
Kd.append(sorptionCoefficient) #mL/g  effective Kd

if (1):
    print "%s\t%g\t%g\t%.1f\t%g\t%g\t%.2f\t%.2f\t%.3e\t%g\t%.5f\t%.5f\t%.1f" \
          % (TI[i], tBeg[i], tEnd[i], tMid, W, B, N[i+1], dN[i], dTotal[i], time[i],
x_Ox[i], x_Re[i], Kd[i])

time.insert(0,0)              # insert time zero values at beginning of lists
x_Ox.insert(0,0)
x_Re.insert(0,1)
Kd.insert(0,Kd_Re)

#main program - - - - -

### time intervals/periods
TI = ['TI01','TI02','TI03','TI04','TI05','TI06','TI07','TI08','TI09','TI10',\
      'TI11','TI12','TI13','TI14','TI15','TI16','TI17','TI18','TI19','TI20',\
      'TI21','TI22','TI23','TI24','TI25','TI26','TI27','TI28','TI29','TI30',\
      'TI31','TI32','TI33','TI34','TI35','TI36','TI37','TI38','TI39','TI40',\
      'TI41','TI42','TI43','TI44']          #time interval labels

tBeg = [0,50,100,150,200,250,300,350,400,450,500,600,700,800,900,1000,\
        1200,1400,1600,1800,2000,2300,2600,2900,3200,3600,4000,4500,5000,\
        5500,6000,6500,7000,7500,8000,8500,9000,9500,10000,\
        11000,12000,15000,20000,50000]      #yr      beginning times

tEnd = [50,100,150,200,250,300,350,400,450,500,600,700,800,900,1000,\
        1200,1400,1600,1800,2000,2300,2600,2900,3200,3600,4000,4500,5000,\
        5500,6000,6500,7000,7500,8000,8500,9000,9500,10000,\
        11000,12000,15000,20000,50000,100000] #yr      ending times

### fractures
#      Physical degradation assumptions:

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t_0 = 10 #yr time at ~0% degradation
t_100 = 10000 #yr time at 100% degradation

B_0 = 10000 #m fracture spacing at ~0% degradation
B_100 = 0.1 #m fracture spacing at 100% degradation

### material properties
# Tc assumptions:
Kd_Ox = 1 #mL/g sorption coefficient for oxidized conditions
Kd_Re = 1000 #mL/g sorption coefficient for reduced conditions

c_Ox_perL = 1.06 #meq e-/L liquid phase oxygen concentration at (oxygen) saturation
c_Ox = c_Ox_perL/1000 #meq e-/mL

# Saltstone properties:
r_Ox = 0.822 #meq e-/g reduction capacity
n = 0.58 #- porosity
D_e = 1.e-7 #cm2/s effective diffusion coefficient
rho_s = 2.4 #g/cm3 solid density
rho_b = (1-n)*rho_s #g/cm3 bulk density

### facility geometry
# Vault4 nominal dimension:
W = 60 #m width
minN = 2 #- minimum number of fracture faces (typically 0, 1 or 2)

### potential overrides
#Kd_Ox = 0.8 #moderate cement
#Kd_Re = 5000

#Kd_Ox = 0.5 #aged cement
#Kd_Re = 5000

#t_100 = 10.1 #wall?
#r_Ox = 0.240
#W = 0.2
#minN = 1

### effective Kd
time = []
x_Ox = []
x_Re = []
Kd = []
effectiveKd(TI, tBeg, tEnd,\
            t_0, t_100, B_0, B_100,\
            Kd_Ox, Kd_Re, n, D_e, c_Ox, r_Ox, rho_b,\
            W, minN,\
            time, x_Ox, x_Re, Kd)

### print results
if (1):
    TI2 = TI
    TI2.insert(0,'TI00')
    print ""
    print "TI\ttime\tx_Ox\tKd"
    for i in range(len(Kd)):
        print "%s\tg\t%.3f\t%.1f" % (TI2[i], time[i], x_Ox[i], Kd[i])

### print DISTRIBUTION command
if (1):

```

```
Species = 'C'  
Zone = 'MyZone'  
pH = 'Moderate'  
print ""  
print "DISTribution of %s in ID=%s, fcn of TIME, TABLE of %g pts: !%s" % (Species, Zone,  
len(Kd), pH)  
for i in range(len(Kd)):  
    print "(%g,%1f)" % (time[i], Kd[i])
```