

ESTIMATED LONGEVITY OF REDUCING ENVIRONMENTS IN GROUTED SYSTEMS FOR RADIOACTIVE WASTE DISPOSAL

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ABSTRACT

A key factor determining the release and transport of redox-sensitive radioelements from grouted, near-surface, low-activity waste disposal facilities at U.S. Department of Energy (DOE) sites is the redox potential of the cement-based material. Published studies have shown that a reducing chemical environment mitigates the release and transport of redox-sensitive radioelements from grouted systems. At DOE low-activity waste disposal sites, blast furnace slag is added to the grout formulation to impose an initially reducing chemical condition on the grouted system. However, there is uncertainty regarding the long-term persistence of the reducing capabilities of the slag-bearing grout. The objective of this study is to estimate how long reducing conditions could persist in near-surface slag-bearing grouted systems for radioactive waste disposal. The oxidant of most concern is oxygen (O_2)—in the gas phase or dissolved in infiltrating water—which could react with the blast furnace slag and decrease the grout reductive capacity. The study used a numerical model representing oxygen transport in fractures and porous grout to assess the persistence of reducing conditions for a range of hydrological conditions, fracturing scenarios, and grout parameter values. The results indicate that for a wide range of hydrological conditions, oxygen concentrations in through-going vertical fractures and conduits in subsurface vaults and tanks are expected to be maintained at or near the levels of the surrounding soil by a combination of gas-phase diffusion and liquid-phase advection. This is because of the relatively slow rate of diffusion in the pore space of the intact grout, which becomes the rate-limiting process for oxygen loss to the oxidation reaction. For the long timeframes of interest in performance assessments, transport processes in the fractures can easily resupply the fractures with oxygen from the surrounding soil. Because diffusion in the pore space of intact grout material is the rate-limiting process for grout oxidation, detailed process-level models coupling fracture transport processes with matrix diffusion and chemical reactions can be avoided. Simpler models coupling oxygen diffusion and grout oxidation reaction can be used instead, with fractures representing internal boundary conditions with specified oxygen concentrations.

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EQUATION PARAMETERS AND UNITS

α	flow-focusing factor [-]
η	fracture permeability empirical reduction factor
Ω_l	liquid-phase flux [meq e ⁻ /(m ² -yr)]
Ω_g	gas-phase flux [meq e ⁻ /(m ² -yr)]
ϕ	matrix porosity [-]
ϕ_f	fracture internal porosity [-]
$\psi_{F \rightarrow M}$	oxygen transfer rate from fracture to matrix [meq e ⁻ /(m ³ -yr)]
ρ_{grout}	grout bulk density [kg/m ³]
τ_l	liquid-phase tortuosity factor [-]
τ_g	gas-phase tortuosity factor [-]
b	fracture aperture [m]
C_p	oxygen concentration in phase p in the fracture [meq e ⁻ /m ³]
C'	oxygen concentration in the matrix pore water [meq e ⁻ /m ³]
D_e	effective diffusion coefficient in the matrix [m ² /yr]
D_l	free-water diffusion coefficient [m ² /yr]
D_g	free-gas diffusion coefficient [m ² /yr]
H	dimensionless Henry's law constant [-]
k	grout oxidation rate constant [m ³ /(yr meq e ⁻)]
k_{rl}	relative permeability to water [-]
K_f	fracture saturated hydraulic conductivity [m/yr]
ℓ	fracture spacing [m]
q_{in}	Darcy velocity of water arriving at the top of grout-filled tank [m ³ /(m ² -yr)]
q_l	liquid Darcy velocity in the fracture [m/yr]
q_g	gas Darcy velocity in the fracture [m/yr]
r	waste tank radius [m]
R	reductant concentration in the grout [meq e ⁻ /kg-solid]
S_l	liquid saturation [-]
S_g	gas saturation [-]
S_{lr}	residual liquid saturation [-]
S_{gr}	residual gas saturations [-]
t	time [yr]
T	temperature [K]
x	spatial coordinate in horizontal direction (perpendicular to fracture) [m]
z	spatial coordinate in vertical direction [m]
L	height of tank and length of vertical fracture [m]

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT DATA

DATA: All CNWRA-generated data contained in this report meet quality assurance requirements described in the Geosciences and Engineering Division Quality Assurance Manual. Sources of other data should be consulted for determining the level of quality of those data. The work presented in this report is documented in Scientific Notebook 986E (Painter, 2009).

ANALYSES AND CODES: Analyses contained in this report were generated using custom scripts within the commercial software Mathematica™ (Wolfram Research, Inc., 2005). The scripts are documented in Scientific Notebook 986E in accordance with procedures described in the Geosciences and Engineering Division Quality Assurance Manual.

References:

Painter, S. "Modeling Longevity of Grout Reducing Conditions." Electronic Scientific Notebook 986E. San Antonio, Texas: CNWRA. 2009.

Wolfram Research, Inc. "Mathematica™." Version 5.2. Champaign, Illinois: Wolfram Research, Inc. 2005.

1 INTRODUCTION

The ability of cement-based materials (e.g., grout) to serve as a barrier to groundwater influx and to radionuclide release and transport is an important factor in U.S. Department of Energy (DOE) performance assessments that are conducted to demonstrate tank closure and low-activity waste disposal in near-surface disposal facilities will meet the appropriate performance objectives. In these performance assessments, assumptions are made regarding the physical integrity and chemical condition of the cement-based material. For redox-sensitive radioelements (e.g., technetium and selenium), a key factor determining their release and transport is the redox potential of the cement-based material (DOE-Idaho, 2003; Washington Savannah River Company Site Regulatory Integration and Planning, 2008; Pabalan, et al., 2009). Various studies have demonstrated the importance of a reducing chemical environment to mitigating the release of redox-sensitive radioelements from grouted systems. For example, leaching of technetium and chromium from saltstone was effectively reduced when blast furnace slag was added to the saltstone formulation (Langton, 1987). Brodda (1988) conducted leaching experiments indicating that blast furnace slag cement spiked with Tc-99 retained 99.9 percent of the technetium after 500 days of leaching in simulated medium-level waste solution. A long-term lysimeter study conducted at the Savannah River Site showed that the addition of slag to the saltstone grout formulation essentially prevented Tc-99 leaching from the waste form (Cook and Fowler, 1992). Gilliam, et al. (1990) demonstrated that technetium leachability is decreased by several orders of magnitude by the addition of blast furnace slag to the grout. More recently, Aloy, et al. (2007) conducted leaching tests showing that blast furnace slag can effectively decrease the mobility of technetium even in the presence of a concentrated salt solution.

The ability of blast furnace slag to reduce the release of redox-sensitive radioelements has been ascribed to the presence of sulfide sulfur (Atkins and Glasser, 1992). Hydration of the slag in the grout mixture releases sulfide species into the pore fluid, predominantly as S^{2-} and possibly with a small contribution from SO_3^{2-} and $S_2O_3^{2-}$ (Atkins and Glasser, 1992), which impose a strongly reducing redox potential on the system. Various investigators have reported measured redox potentials of fluids that were reacted with slags and slag-bearing, cement-based materials; these are summarized in Table 1-1. At the low Eh conditions imposed by the slag, the solubilities of redox-sensitive elements tend to be low (Angus and Glasser, 1985; Pickett, et al., 2009), and the sulfide species released into solution by slag hydration can chemically bind contaminants as insoluble species. For example, technetium is believed to react with the sulfide to form Tc_3S_{10} (Lukens, et al., 2005) or Tc_2S_7 (Liu, et al., 2007), reducing the release of technetium through groundwater pathways.

An important assumption in DOE performance assessments is that the amount of blast furnace slag in the grout formulation and the sulfide concentration in the slag are sufficient to impose a reducing environment. However, existing national standards do not specify the sulfide content of slag, except as a maximum, and commercial blast furnace slag may vary in the amount of sulfide. ASTM C-989 (ASTM International, 2009) sets a maximum limit of 2.5 weight percent with respect to the sulfide content, but no minimum sulfide content is specified in the standard. Most North American and European slag contains sulfur (as sulfide) in the range 0.6 to 1.0 weight percent (Pabalan, et al., 2009). However, the modern tendency to use preprocessed iron feed stocks and “clean” coals results in the sulfur content of modern slag tending toward lower values. As a consequence, there are uncertainties in the amount of sulfide sulfur reserve and in the reductive capacity of slag-bearing grouts. These uncertainties can be reduced by conducting laboratory measurements to confirm the slag sulfide content (e.g., Waldron, 2007) or the reductive capacity of the grout (e.g., Kaplan, et al., 2008). Reported reductive capacity of slags and slag-bearing, cement-based materials is summarized in Table 1-2.

Table 1-1. Reported Redox Potential (Eh) of Fluids Reacted With Blast Furnace Slag and Slag-Bearing Cement-Based Material. For Comparison, Eh Values of Fluids Reacted With Ordinary Portland Cement, Fly Ash, Savannah River Site Sediment, and Saltstone Simulant Also Are Listed.

Reference	Measured Redox Potential (Eh, mV)*	Experimental Condition
Angus and Glasser (1985; Table V)†	+82 -315	OPC‡ BFS§ mixed with Ca(OH) ₂ in the ratio 10:1
Angus and Glasser (1985; Table VI)†	+82 +79 +68 +35 -240 -269 -330 -259	100:0 OPC:BFS 75:25 OPC:BFS 50:50 OPC:BFS 25:75 OPC:BFS 15:85 OPC:BFS 10:90 OPC:BFS 5:95 OPC:BFS¶ 2.5:97.5 OPC:BFS¶
Angus and Glasser (1985; Table VIII)†	-227 -202	15:85 OPC:BFS ; matured 25 days at 20 °C 15:85 OPC:BFS; matured 25 days at 40 °C
Gilliam, et al. (1988)#	+450 +450 -250	Fly ash OPC BFS
Atkins and Glasser (1992)**	0 to +100 -305±35††	100:0 OPC:BFS 15:85 OPC:BFS
Kaplan and Hang (2007)‡‡	+196±3 -247±1	Savannah River Site sediment BFS sample
Kaplan, et al. (2008)§§	-750	Saltstone simulant

*Versus standard hydrogen electrode

†Angus, M.J. and F.P. Glasser. "The Chemical Environment in Cement Matrices." Scientific Basis for Nuclear Waste Management IX. Proceedings of the Materials Research Society Symposium Vol. 50. L.O. Werme, ed. Warrendale, Pennsylvania: Materials Research Society. 1985.

‡OPC—ordinary Portland cement

§BFS—blast furnace slag

||Mass ratio of OPC to BFS

¶With 0.5 wt% NaOH solution added to ensure setting

#Gilliam, T.M., R.D. Spence, B.S. Evans-Brown, I.L. Morgan, J.L. Shoemaker, and W.D. Bostock. "Performance Testing of Blast Furnace Slag for Immobilization of Technetium in Grout." Proceedings from Spectrum '88—International Topical Meeting on Nuclear and Hazardous Waste Management, Pasco, Washington, September 11–15, 1988. LaGrange, Illinois: American Nuclear Society. 1988.

**Atkins, M. and F.P. Glasser. "Application of Portland Cement-Based Materials to Radioactive Waste Immobilization." *Waste Management*. Vol. 12. pp. 105–131. 1992.

††Mean and standard deviation of six samples aged up to 10 months

‡‡Kaplan, D.I. and T. Hang. "Estimated Duration of the Subsurface Reduction Environment Produced by the Saltstone Disposal Facility on the Savannah River Site." Rev. 0. WSRC-STI-2007-00046. Aiken, South Carolina: Westinghouse Savannah River Company. 2007

§§Kaplan, D.I., K. Roberts, J. Coates, M. Siegfried, and S. Serkiz. "Saltstone and Concrete Interactions With Radionuclides: Sorption (Kd), Desorption, and Reduction Capacity Measurements." SRNS-STI-2008-00045. Aiken, South Carolina: Savannah River National Laboratory. 2008.

Table 1-2. Reported Reductive Capacity of Slag and Slag-Bearing Cement-Based Materials. For Comparison, Measured Reductive Capacity of Other Materials Also Are Listed.

Reference	Measured Reductive Capacity (meq e ⁻ /g solid)*	Experimental Condition
Angus and Glasser (1985; Table VII)†	0.0959 0.0343 1.14, 1.10	OPC‡ Fly ash BFS§(two samples)
Lukens, et al. (2005)	0.82	BFS¶
Atkins and Glasser (1992)#	0.1 1.0 0.6	100:0 OPC:BFS 0:100 OPC:BFS; unhydrated 15:85 OPC:BFS; hydrated; aged for 90 days
Aloy, et al. (2007)**	4.79††	BFS
Kaplan and Hang (2007)‡‡	0.0051§§ 0.037§§	Savannah River Site sediment BFS sample
Kaplan, et al. (2005)	0.817	BFS
Kaplan, et al. (2008)¶¶¶	0.832±0.005 0.240±0.031 0.822±0.008 0.0244±0.0007 0.081±0.012 0.086±0.010	BFS Savannah River Site Vault 2 concrete with 10 wt% BFS Saltstone stimulant with 23 wt% BFS Savannah River Site red sediment Savannah River Site sandy sediment Savannah River Site 50-yr old cement

*Unless otherwise indicated, reductive capacity was measured with the method of Angus and Glasser (1985), which used Ce(IV) as an oxidizing agent

†Angus, M.J. and F.P. Glasser. "The Chemical Environment in Cement Matrices." Scientific Basis for Nuclear Waste Management IX. Proceedings of the Materials Research Society Symposium Vol. 50. L.O. Werme, ed. Warrendale, Pennsylvania: Materials Research Society. 1985.

‡OPC—ordinary Portland cement

§BFS—blast furnace slag

||Lukens, W.W., J.I. Bucher, D.K. Shuh, and N.M. Edelstein. "Evolution of Technetium Speciation in Reducing Grout." *Environmental Science and Technology*. Vol. 39. pp. 8,064–8,070. 2005.

¶Mass ratio of OPC to BFS

#Atkins, M. and F.P. Glasser. "Application of Portland Cement-Based Materials to Radioactive Waste Immobilization." *Waste Management*. Vol. 12. pp. 105–131. 1992.

**Aloy, A., E.N. Kovarskaya, J.R. Harbour, C.A. Langton, and E.W. Holtzscheiter. "Pretreatment of Tc-Containing Waste and Its Effect on Tc-99 Leaching From Grouts." Scientific Basis for Nuclear Waste Management XXX. Proceedings of the Materials Research Society Symposium Vol. 985. D.S. Dunn, C. Poinssot, and B. Begg, eds. Warrendale, Pennsylvania: Materials Research Society. 2007

††Measured using KMnO₄ as an oxidizing agent

‡‡Kaplan, D.I. and T. Hang. "Estimated Duration of the Subsurface Reduction Environment Produced by the Saltstone Disposal Facility on the Savannah River Site." Rev. 0. WSRC–STI–2007–00046. Aiken, South Carolina: Westinghouse Savannah River Company. 2007

§§Measured using Cr(VI) as an oxidizing agent

|||Kaplan, D.I., T. Hang, and S.E. Aleman. "Estimated Duration of the Reduction Capacity Within a High-Level Waste Tank (U)." Rev. 0. WSRC–RP–2005–01674. Aiken, South Carolina: Westinghouse Savannah River Company. 2005.

¶¶¶Kaplan, D.I., K. Roberts, J. Coates, M. Siegfried, and S. Serkiz. "Saltstone and Concrete Interactions With Radionuclides: Sorption (K_d), Desorption, and Reduction Capacity Measurements." SRNS-STI-2008-00045. Aiken, South Carolina: Savannah River National Laboratory. 2008.

There is also uncertainty regarding the long-term persistence of the reducing capabilities of the slag-bearing grout. The oxidant of most concern is oxygen (O_2), which could react with and decrease the reductive capacity of slag. Oxygen can be present in the gas phase or dissolved in infiltrating water, and the relative importance of each phase will depend on the flow pathways through the grout, the hydrologic saturation condition, and the flow rate of infiltrating water. The presence of cracks or conduits could facilitate oxygen influx into the grouted system, but slow oxygen diffusion into the grout matrix could limit redox changes to areas along the interface of the crack or conduit with the grout. Little information is available to assess the long-term persistence of reducing conditions of grouted systems for radioactive waste disposal. Thus, degradation experiments and modeling studies are warranted to address this issue.

The objective of this study is to estimate how long reducing conditions could exist in shallow subsurface slag-bearing grouted systems for radioactive waste disposal. The study used a numerical model representing oxygen transport in fractures and porous grout to assess the lifetime of reducing conditions for a range of hydrological conditions, fracturing scenarios, and grout parameter values.

2 MODEL FOR OXYGEN TRANSPORT IN FRACTURED, POROUS GROUT

This study considers a system composed of a water-saturated porous grout and through-going vertical fractures that are filled with a combination of air and water. For simplicity, parallel fractures with constant spacing are considered.¹ Water is modeled as being mobile in the fractures but immobile in the grout pore space because of the large permeability contrasts between fractures and porous matrix. The fractures allow vertical transport of oxygen by gas-phase diffusion and liquid-phase advection and diffusion/dispersion. Diffusion in the grout pore water allows dissolved oxygen to reach and oxidize the reducing grout.

2.1 Hydrological Conditions

Liquid flow rates and water saturations in the fractures are needed to model the hydrological conditions of a fractured, grouted system. Given boundary conditions and assumptions about the size, location, and permeability of the fractures, detailed modeling of unsaturated flow could be used to estimate these hydrological conditions. Rice and Walton (2006) performed detailed modeling of flow in the vicinity of degraded concrete vaults, which were assumed to have hydraulic properties of sand. They observed that in the absence of an engineered low-permeability clay layer above a vault and for infiltration rates of 10 mm/yr and greater, nearly all infiltrating water passes through the degraded vault. Their result combined with an additional assumption that the relatively weak capillary suction typical for fractures would prevent ponding of water at the bottom of a fracture suggests a simple abstraction of the hydrological process. This abstraction allows a broad range of scenarios to be assessed without the computational burden of detailed numerical flow models.

Given the Darcy velocity, q_{in} [$m^3/(m^2\text{-yr})$], for water arriving at the top of the grout-filled tank, the Darcy velocity in the fracture, q_f [$m^3/(m^2\text{-yr})$], may be approximated as

$$q_f = \alpha q_{in} \quad (2-1)$$

where α [-] is a flow-focusing factor that depends on the scenario under consideration. With equally spaced parallel fractures and no seepage diversion, the flow-focusing factor, α , is

$$\alpha = \ell/b \quad (2-2)$$

where ℓ [m] is the fracture spacing and b [m] is the fracture aperture. Alternatively, if a single, continuous conduit running along the outer circumference of a tank is assumed (e.g., as a result of grout shrinkage causing the hardened grout to separate from the tank wall), the flow-focusing factor is

$$\alpha = r/2b \quad (2-3)$$

where r [m] is the radius of the tank. For vertical, unsaturated gravity flow and no sources of water within the fractures, the liquid saturation within the fracture can be found by equating the fracture Darcy velocity with the fracture hydraulic conductivity

¹In real grouted systems, fractures would be considerably more complex in terms of spacing, aperture size, distribution, and orientation than the idealized parallel fractures considered in this study. Mesoscale experiments (Walter, et al., 2009) also indicate that preferential flow paths for oxygen transport can occur in the form of annular gaps around pipes and other embedded structures due to grout shrinkage.

$$\alpha q_{in} = K_f k_r(S_l) \quad (2-4)$$

where K_f [m/yr] is the fracture saturated hydraulic conductivity, k_r [-] is the relative permeability to water, and S_l [-] is the liquid saturation. Solving for S_l and noting that αq_{in} cannot exceed the fracture saturated hydraulic conductivity K_f unless the fracture is water-filled,

$$S_l = k_r^{-1} \left(\min \left(\frac{\alpha q_{in}}{K_f}, 1 \right) \right) \quad (2-5)$$

Little is known about relative permeability in fractures. Persoff and Pruess (1995) measured gas- and liquid-phase relative permeability and cross-plotted the two permeabilities to demonstrate phase interference. However, they did not independently measure water saturation. Diomampo (2001) measured relative permeabilities in horizontal fractures and showed that liquid-phase relative permeability was reasonably approximated by a Corey-type fit

$$k_r(S_l) = \left[\frac{S_l - S_{lr}}{1 - S_{lr} - S_{gr}} \right]^n \quad (2-6)$$

where the term in brackets is the reduced saturation [-], n [-] has a value of 1.75, and the residual liquid and gas saturations, S_{lr} [-] and S_{gr} [-], are 0.135 and 0, respectively.

A relationship between fracture aperture, b , and fracture saturated hydraulic conductivity, K_f , is also required. With b in m and K_f in m/yr, the cubic law for parallel-plate fractures leads to

$$K_f \approx 2.63 \times 10^{13} b^2 \quad (2-7)$$

However, this expression tends to overestimate the permeability of natural rough-wall fractures. Thus, the cubic law is modified here as

$$K_f = \eta 2.63 \times 10^{13} b^2 \quad (2-8)$$

where $\eta < 1$ is an empirical reduction factor.

2.2 Oxygen Transport and Grout Oxidation

The evolution of the oxygen concentration in the grout is represented by coupling one-dimensional advection-dispersion in the fracture with one-dimensional diffusion in the perpendicular direction representing diffusion into the porous grout. Rather than model the detailed oxidation-reduction reactions, the approach of Kaplan, et al. (2005) and Kaplan and Hang (2007) is used here. In this approach, the oxidation-reduction reaction is written as an effective reaction that consumes oxygen and grout-reducing equivalents and produces oxidized grout:



where

O_2 — oxygen (in air or dissolved in water)
 R — reduced grout
 RO_2 — oxidized grout

Let

$C_l(z, t)$ — liquid-phase oxygen concentration in the fracture [meq e⁻/m³]
 $C_g(z, t)$ — gas-phase oxygen concentration in the fracture [meq e⁻/m³]
 $C'(x, z, t)$ — oxygen concentration in the matrix pore water [meq e⁻/m³]
 $R(x, z, t)$ — reductant concentration in the grout [meq e⁻/kg-solid]
 x — spatial coordinate in horizontal direction (perpendicular to fracture) [m]
 z — spatial coordinate in vertical direction [m]
 t — time [yr]
 L — length of fracture [m]

The oxygen conservation equation in the fractures is

$$\phi_f S_l \frac{\partial C_l}{\partial t} + \phi_f S_g \frac{\partial C_g}{\partial t} + \frac{\partial}{\partial z} (\Omega_l + \Omega_g) = -\psi_{F \rightarrow M} \quad (2-10)$$

where $\psi_{F \rightarrow M}$ [meq e⁻/(m³-yr)] is the oxygen transfer rate from fracture to matrix and the fluxes along the fractures are defined by

$$\Omega_l = -\phi_f S_l \tau_l D_l \frac{\partial C_l}{\partial z} + q_l C_l \quad (2-11)$$

$$\Omega_g = -\phi_f S_g \tau_g D_g \frac{\partial C_g}{\partial z} + q_g C_g \quad (2-12)$$

where

Ω_l — liquid-phase fluxes [meq e⁻/(m²-yr)]
 Ω_g — gas-phase fluxes [meq e⁻/(m²-yr)]
 D_l — free-water diffusion coefficient [m²/yr]
 D_g — free-gas diffusion coefficient [m²/yr]
 τ_l — liquid-phase tortuosity factor [-]
 τ_g — gas-phase tortuosity factor [-]
 q_l — liquid Darcy velocity [m/yr]
 q_g — gas Darcy velocity [m/yr]
 S_g — gas saturation [-] (1 - S_l)
 ϕ_f — fracture internal porosity (1 for an open fracture containing no sediment).

The gas tortuosity factor is based on the Millington and Quirk (1961) relationship

$$\tau_g = \phi_f^{1/3} S_g^{7/3} \quad (2-13)$$

Similarly, the liquid tortuosity factor is related to porosity and liquid saturation by Archie's law

$$\tau_l = \phi_f^m S_l^n \quad (2-14)$$

The exponents m and n are typically around 0.3 and 1.0, respectively.

Using Henry's law

$$C_l = H C_g \quad (2-15)$$

where H [-] is the dimensionless Henry's law constant $\{3.2 \times 10^{-2}$ for oxygen at 298 K}, the conservation equation becomes

$$\phi_f S_{eff} \frac{\partial C_l}{\partial t} + q_{eff} \frac{\partial C_l}{\partial z} - \phi_f D_{eff} \frac{\partial^2 C_l}{\partial z^2} = -\psi_{F \rightarrow M} \quad (2-16)$$

where

$$D_{eff} = \tau_l S_l D_l + H^{-1} \tau_g S_g D_g \quad (2-17)$$

$$S_{eff} = (S_l + H^{-1} S_g) \quad (2-18)$$

$$q_{eff} = q_l + H^{-1} q_g \quad (2-19)$$

The fracture-to-matrix oxygen transfer rate, $\psi_{F \rightarrow M}$, is proportional to the oxygen concentration gradient in the matrix pore water at the fracture wall

$$\psi_{f \rightarrow m} = \frac{\phi}{b} D_e \left. \frac{\partial C'}{\partial x} \right|_{x=0} \quad (2-20)$$

where ϕ [-] is the matrix porosity, and D_e [m²/yr] is the effective oxygen diffusion coefficient in the matrix.

The oxygen conservation equations in the matrix are

$$\phi \frac{\partial C'}{\partial t} - \phi D_e \frac{\partial^2 C'}{\partial x^2} = -k C' R \rho_{grout} \quad (2-21a)$$

$$\frac{\partial R}{\partial t} = -k C' R \quad (2-21b)$$

where ρ_{grout} [kg/m³] is the bulk density of the grout, and k [m³/(yr meq e⁻)] is the grout oxidation rate constant. These partial differential equations are solved in this study using the NDSolve

routine of the Mathematica™ software (Wolfram Research, Inc., 2005), which uses the numerical method of lines with sophisticated adaptive algorithms for error control. The boundary and initial conditions are

$$\left. \frac{\partial C'}{\partial x} \right|_{x=\ell/2} = 0 \quad (2-22a)$$

$$C'(x = 0, z, t) = C_l(z, t) \quad (2-22b)$$

$$C_l(z = 0, t) = C_0 \quad (2-22c)$$

$$C_l(z = L, t) = C_0 \quad (2-22d)$$

$$C_l(z, t = 0) = 0 \quad (2-22e)$$

$$C'(x, z, t = 0) = 0 \quad (2-22f)$$

$$R_0(x, z, t = 0) = R_0 \quad (2-22g)$$

2.3 Examples

The following grout parameters Kaplan, et al. (2005) reported are used for the reference case:

$$D_e = 1.58 \times 10^{-5} \text{ m}^2/\text{yr}$$

$$R_0 = 49.8 \text{ meq e}^-/\text{kg}$$

$$\rho_{\text{grout}} = 1,700 \text{ kg/m}^3$$

$$\phi = 0.46$$

$$C_0 = 1.0 \times 10^3 \text{ meq e}^-/\text{m}^3$$

$$q_{\text{in}} = 0.4 \text{ m/yr}$$

The gas-phase diffusion coefficient, D_g , for oxygen is a handbook value. Weast, et al. (1986) give $0.18 \text{ cm}^2/\text{s}$ at 0°C . Using gas-phase diffusion coefficients proportional to temperature, T [K], as $T^{3/2}$ (e.g., Bird, et al., 2006), D_g is calculated as $0.20 \text{ cm}^2/\text{s}$ or $647 \text{ m}^2/\text{yr}$ at 25°C . Liquid-phase dispersion is assumed to be negligible compared to gas-phase diffusion.

Kaplan, et al. (2005) noted that Eq. (2-9) is a fast reaction (i.e., not subject to kinetic limitations). Under these situations, the exact value of the rate constant does not affect the modeling results as long as the rate constant is sufficiently large to make the reaction rates fast compared to characteristic transport rates. Preliminary numerical experimentation revealed that a grout oxidation rate constant, k , equal to $10^{-3} \text{ m}^3/(\text{yr meq e}^-)$ or larger is sufficient to model a fast reaction. That value is used here.

For illustration purposes, a fracture aperture of 0.3 mm and fracture spacing of 0.3 m are assumed, which implies a flow-focusing factor of 10^3 . Using the cubic law with $\eta = 0.1$, the saturated hydraulic conductivity is $7.5 \times 10^{-3} \text{ m/s}$, which is in the range of values for clean gravel and a factor of 750 larger than that assumed by Kaplan, et al. (2005). The ratio of Darcy velocity to saturated hydraulic conductivity q/K_f is approximately 1.7×10^{-3} . This value is much

less than 1. Thus, the liquid saturation should be close to the residual saturation, independent of the relative permeability function. A residual saturation of 0.1 is assumed in this study, in line with Diomampo's (2001) value of 0.135.

Oxygen concentrations versus depth along the fracture at different times are shown in Figure 2-1 for several different combinations of fracture aperture and spacing (see Table 2-1). These modeling cases include both open fractures and wide fractures filled with sediment. In producing this plot, the boundary conditions at the top and bottom of the fracture were not imposed instantaneously, but were allowed to ramp linearly from 0 to 10^3 meq e^-/m^3 over a 5-year simulation time for numerical reasons.

In all eight modeling cases listed in Table 2-1, the oxygen concentration in the fracture rapidly reaches a steady-state profile that is not significantly different from the imposed boundary conditions. Oxygen loss to the matrix is slow enough that the fracture can be resupplied by a combination of gas-phase diffusion and liquid-phase advection. Modeling cases C, D, E, G and H exhibit asymmetry in the profile. When diffusion is dominant over advection, the profile is nearly symmetrical in depth because the same boundary condition is imposed on the top and bottom. The asymmetry evident in modeling cases C, D, E, G and H is caused by advection being significant relative to diffusion. Case B has the lowest oxygen concentration and the slowest approach to a steady-state profile. The combination of parameters for this case results in a liquid saturation that is large enough to interfere with gas-phase diffusion but not large enough to create significant advective transport. This situation, in combination with the relatively small fracture aperture, increases the relative rate of oxygen loss to the matrix as compared with the other cases. Case F, which has a value for the liquid saturation similar to that of case B, exhibits a slower approach to steady state because the larger aperture reduces the rate of oxygen transfer to the matrix (Eq. 2-20).

Although significant variation can be seen between the various modeling cases, the main behavior is that oxygen concentrations in the fractures achieve those of the surrounding soil relatively quickly because oxygen transport in the fracture is fast compared with the rates of diffusive loss to the porous grout matrix. In other words, grout oxidation is limited by the diffusion rate in the grout. These calculations demonstrate that diffusion in the grout is the rate-limiting process and, given the timeframes of interest in performance assessments, gas-phase diffusion and liquid-phase advection are sufficient to keep the fracture supplied with oxygen.

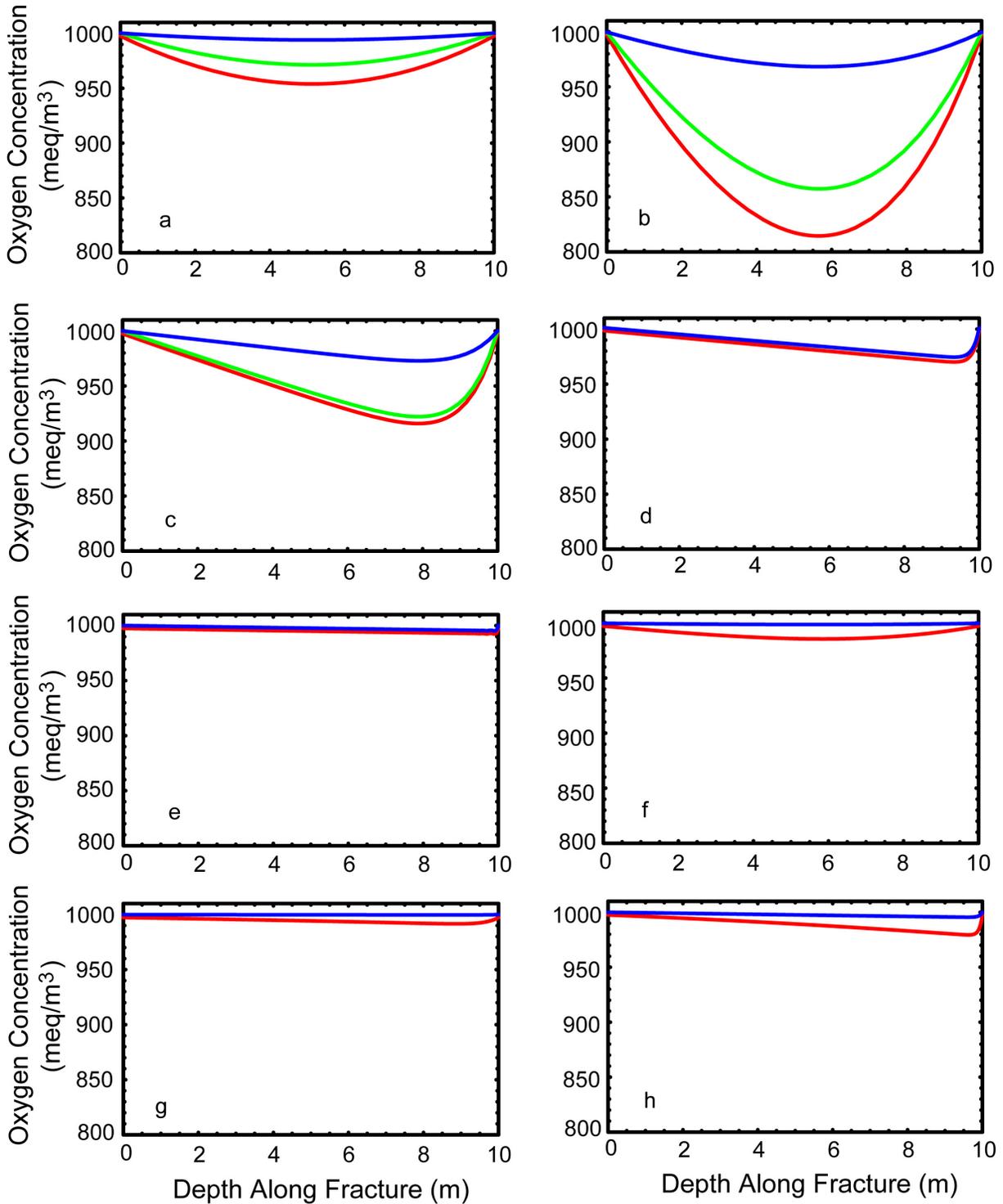


Figure 2-1. Calculated Oxygen Concentration in Through-Going Vertical Fractures Versus Depth Assuming a Coupled Advection/Dispersion and Matrix Diffusion Model. The Red, Green, and Blue Curves Are the Results After 5, 10, and 100 Years, Respectively. The Green Curves Are Hidden Behind the Blue Curves in Figures 2-1(d) Through 2-1(h). In All Cases, the Oxygen Concentration in the Fracture Stays Very Close to That of the Surrounding Soil (1,000 meq e⁻/m³). Table 2-1 Lists the Parameters for the Different Cases.

**Table 2-1. Model Cases Considered When Assessing
Oxygen Content in Fractures (see Figure 2-1)**

Modeling Case	Fracture Aperture, b (mm)	Fracture Spacing, ℓ (m)	Fracture Hydraulic Conductivity Model	Fracture Porosity, ϕ_f (-)	Calculated Saturation in Fracture, S_f
A	0.3	0.3	Cubic law $\eta = 0.1$	1.0	0.15
B	0.1	0.3	Cubic law $\eta = 0.1$	1.0	0.28
C	0.1	1.0	Cubic law $\eta = 0.1$	1.0	0.43
D	0.1	2.0	Cubic law $\eta = 0.1$	1.0	0.57
E	0.1	5.0	Cubic law $\eta = 0.1$	1.0	0.87
F	10	5.0	Sediment filled, $k_f = 10^{-4}$ m/s	0.25	0.31
G	10	20	Sediment filled, $k_f = 10^{-4}$ m/s	0.25	0.58
H	10	5	Sediment filled, $k_f = 10^{-5}$ m/s	0.25	0.80

3 MATRIX DIFFUSION MODEL

The results of the previous section suggest that the longevity of a reducing environment in grouted systems can be studied using a diffusion-only model. In this simplified approach, the oxygen concentration within fractures is prescribed as a boundary condition for a one-dimensional diffusion model. This approximation is valid when the diffusion rate in the grout is small compared to the oxygen transport rate in the fracture. Under these conditions, diffusion in the grout becomes the rate-limiting process and oxygen concentrations in the fractures are maintained at the levels of the soil surrounding the grouted tank or vault.

The conditions under which the diffusion-only model is useful can be estimated by considering characteristic diffusion times and lengths. Clearly, oxidation of the reducing grout is not diffusion limited when the fracture first forms, because unaltered reducing grout will initially be in contact with the oxygen-bearing fractures. At later times, however, oxygen must diffuse through a zone of oxidized grout to reach unaltered reducing grout. If this oxidized zone is sufficiently large, diffusion in the grout becomes the rate-limiting process. Thus, there exists a threshold size Δ for the oxidized zone at which the characteristic transport times in the fracture and in the matrix are equal. The diffusion-only model becomes a useful approximation when this threshold zone is small compared with the fracture spacing $\Delta/\ell \ll 1$.

To relate Δ to physical properties of the grout and fracture, recall that the characteristic length scale (e.g., Crank, 1975) for diffusion in the grout increases with time t as $2\sqrt{t D_e/\phi}$.

Replacing t with the characteristic time for diffusion in the fracture, $L^2 S_{eff}/4D_{eff}$, results in an expression for the threshold size

$$\Delta = L \sqrt{\frac{S_{eff}}{\phi} \frac{D_e}{D_{eff}}} \quad (3-1)$$

Thus, the condition for the pure-diffusion transport model is

$$\frac{L}{\ell} \sqrt{\frac{S_{eff}}{\phi} \frac{D_e}{D_{eff}}} \ll 1 \quad (3-2)$$

For the example calculation in the previous section, Δ is about 2.5 mm, which means the oxygen transport process is limited by diffusion in the grout when the oxidation front has penetrated about 2.5 mm into the grout. This distance is small relative to typical fracture spacing, thus confirming that grout oxidation is limited by the diffusion rate in the grout. Note, however, that these estimates consider gas-phase diffusion only. The numerical modeling results of the previous section reveal that liquid-phase advection becomes significant when the liquid saturation in the fractures becomes large [e.g., note the asymmetry in Figure 2-1(d), (e), (g) and (h)].

With the oxygen concentration at the fracture wall fixed at the value C_0 , one-dimensional diffusion in the pore space governs oxygen transport and, ultimately, oxidation rate of the grout.

The governing equations for oxygen concentration in the grout [Eq. (2-21)] are repeated here for convenience, with the appropriate boundary and initial conditions:

$$\phi \frac{\partial C'}{\partial t} - \phi D_e \frac{\partial^2 C'}{\partial x^2} = -kC'R\rho_{grout} \quad (3-3a)$$

$$\frac{\partial R}{\partial t} = -kC'R \quad (3-3b)$$

$$\left. \frac{\partial C'}{\partial x} \right|_{x=l/2} = 0 \quad (3-3c)$$

$$C'(x=0, z, t) = C_0 \quad (3-3d)$$

$$C'(x, z, t=0) = 0 \quad (3-3e)$$

$$R_0(x, z, t=0) = R_0 \quad (3-3f)$$

As in the previous section, these equations are solved in this study using the NDSolve routine of the Mathematica™ software (Wolfram Research, Inc., 2005).

Oxygen concentrations in the grout pore space and reductant concentrations are shown versus distance from the fracture wall in Figure 3-1 for the reference case conditions and at four different times. The reaction rate constant, k , used here is $0.001 \text{ m}^3/(\text{yr meq e}^-)$, which is 1,000 times slower than the value of $1 \text{ m}^3/(\text{yr meq e}^-)$ Kaplan, et al. (2005) suggested. Even at the slower rate, the reaction rate is much faster than the diffusion rates in the grout. Results in this situation become independent of the reaction rate; the exact value of the reaction rate constant does not affect the result as long as it is sufficiently fast. It is less demanding numerically to use the slower rate.

Because the reaction rate is fast compared with the diffusive transport rate, the oxidation reactions occur in a narrow front that migrates slowly away from the fracture. The rate of penetration of the oxidation front can be estimated as follows. Let $\xi(t)$ denote the position of the oxidizing front measured from the fracture wall. Oxygen molecules will arrive at the oxidizing front at a rate

$$\phi D_e \frac{\partial C'}{\partial x} \approx \phi D_e \frac{C_0}{\xi(t)} \quad (3-4)$$

The molar concentration of reductant ahead of the front is $R_0\rho_{grout}$, and the reductant is thus removed at a rate of $R_0\rho_{grout} \frac{\partial \xi}{\partial t}$. Balancing the reductant removal rate with the oxygen molecule arrival rate gives a differential equation

$$\xi \frac{\partial \xi}{\partial t} = \frac{D_e \phi C_0}{R_0 \rho_{grout}} \quad (3-5)$$

that has the solution

$$\xi(t) = \sqrt{2 \frac{D_e \phi C_0}{R_0 \rho_{grout}} t} \quad (3-6)$$

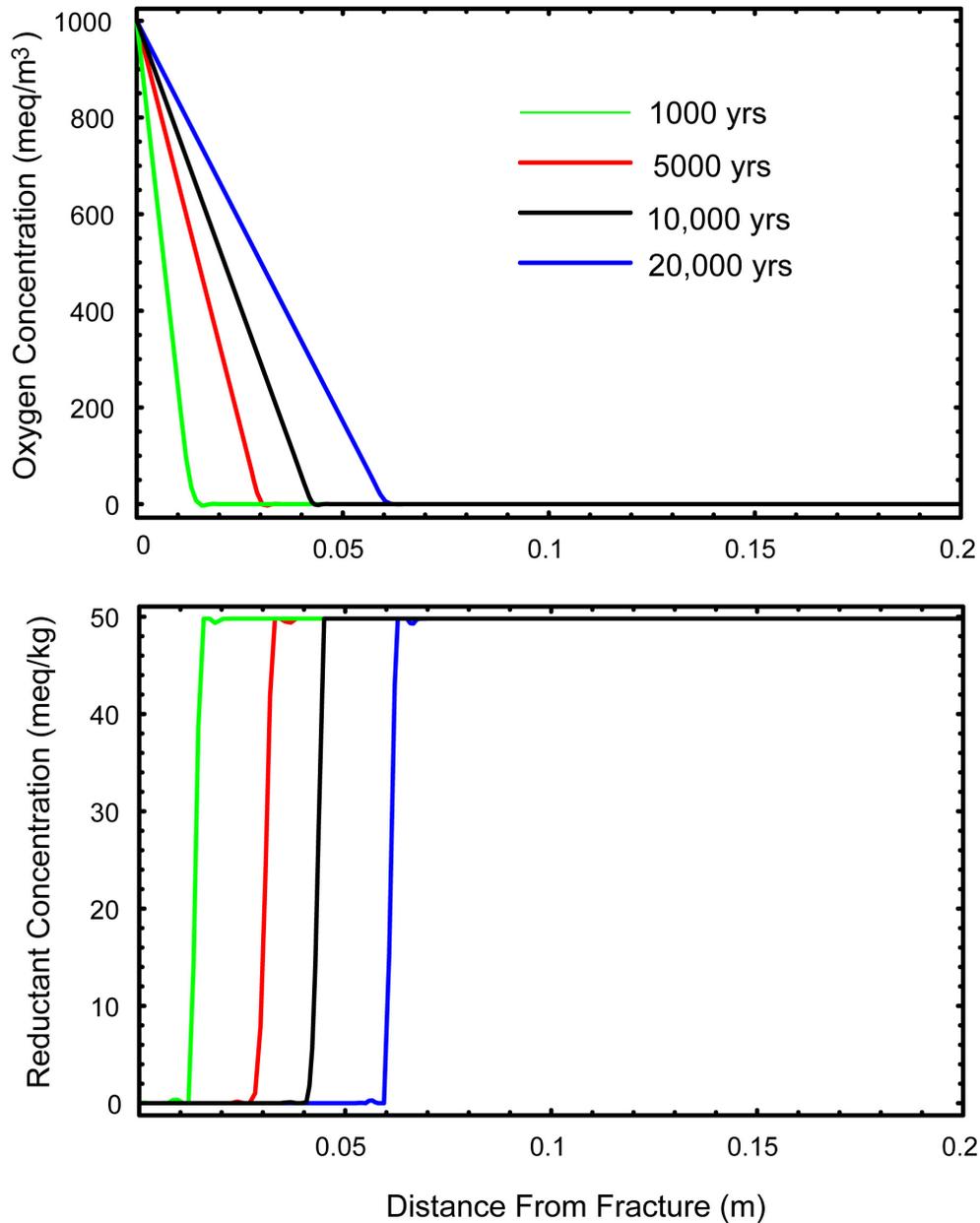


Figure 3-1. Oxygen and Reductant Concentration Versus Distance From the Fracture Calculated by a Diffusion/Reaction Model

Figure 3-2(a) through (d) compares the oxidation front position versus time for several combinations of grout parameters. The curve in each plot is derived from the analytic Eq. (3-6). The numerical model results obtained by solving Eq. (3-3) for the oxidation front position are shown as individual data points in Figure 3-2. Equation (3-6) provides an excellent fit to the numerical results for all combinations considered. Only when the reductive capacity of the grout is reduced to 1/100 of the measured value are deviations from Eq. (3-6) evident.

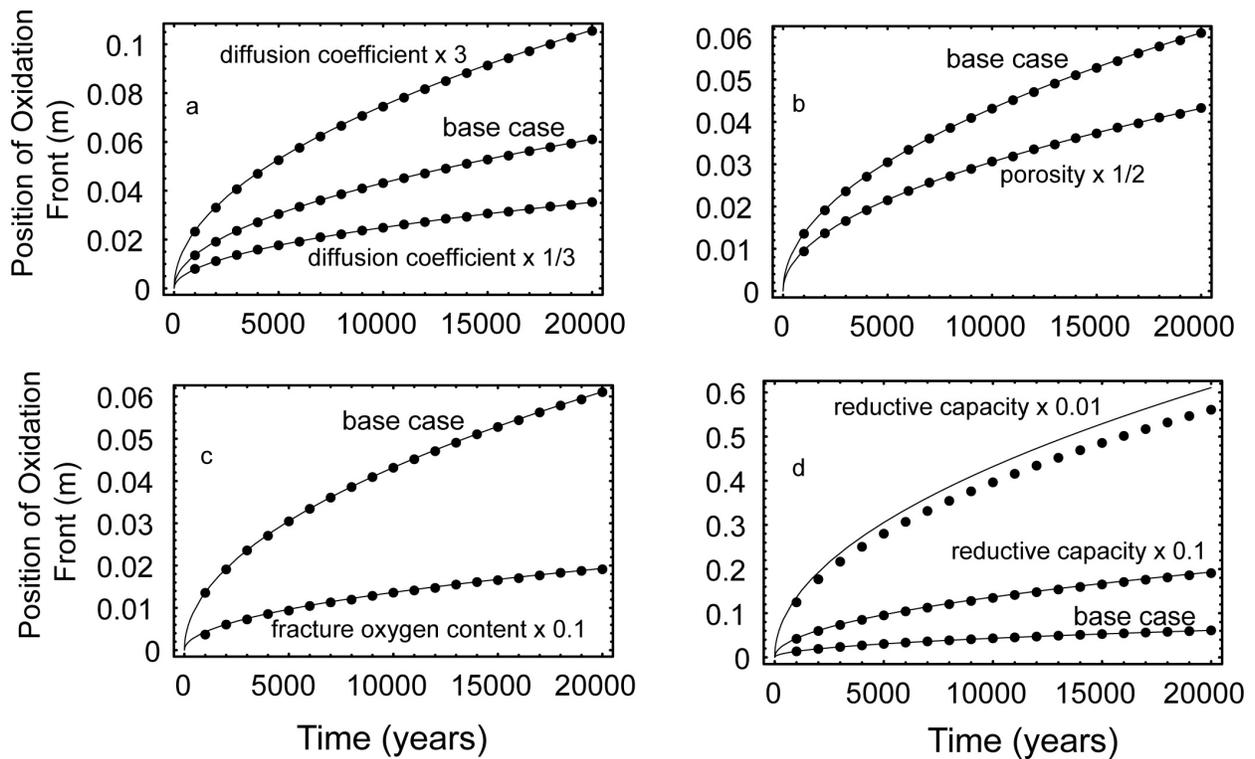


Figure 3-2. Oxidation Front Position Versus Time Calculated by Solving the Diffusion/Reaction System of Eq. (3-3) (Individual Data Points) and by Using the Analytical Eq. (3-6) (Solid Lines). The Individual Plots Show Sensitivity to the Diffusion Coefficient (a), Porosity (b), Oxygen Content in Fracture (c), and Grout Initial Reductive Capacity (d).

4 LONGEVITY OF REDUCING CONDITIONS

4.1 Reference Case

Equation (3-6) provides a convenient alternative to numerical modeling for the purposes of estimating the volume fraction of a tank or vault that is oxidized as function of time. For parallel fractures in an infinite medium, the fraction, f , oxidized may be estimated from the equation

$$f = \frac{2\xi(t)}{\ell} = \frac{2}{\ell} \sqrt{2 \frac{D_e \phi C_0}{R_0 \rho_{\text{grout}}} t} \quad (4-1)$$

Results assuming reference case parameters are shown in Figure 4-1 for fracture spacings of 0.1, 1, and 10 m. For comparison, the three-fracture scenario of Kaplan, et al. (2005) has a fracture spacing of about 5 m. Kaplan, et al. (2005) estimated 8 percent of the reducing grout is oxidized at 10,000 years and approximately 30 percent is oxidized at 50,000 years. Using Eq. (4-1) and the same parameter values, it is estimated that 1.7 percent of the reducing grout is oxidized at 10,000 years and 3.9 percent at 50,000 years. It is important to note that close agreement with the Kaplan et al. (2005) results is not to be expected because the Kaplan, et al. (2005) model is two-dimensional and results in significant oxidation (e.g., approximately 23 percent at 50,000 years) in the absence of cracks due to diffusion from the top and sides.

4.2 Sensitivity Analysis

The most uncertain parameters in Eq. (4-1) are the diffusion coefficient, D_e , the reductive capacity, R_0 , and the spacing, ℓ . Kaplan, et al. (2005) used a D_e value of 1.58×10^{-5} m²/yr for the oxygen diffusion coefficient in reducing grout. This value is the same as that Phifer, et al. (2006) recommended for the nominal D_e value of saltstone. Measured saltstone D_e values range over approximately one order of magnitude (Phifer, et al., 2006). It should be noted that the measured values are for intact laboratory samples of grout. Grout emplaced in the field may have higher effective diffusivities than considered in the analysis presented in this report due to processes such as bleed and segregation, which can produce layers of increased porosity and permeability within the grout mass, or to the formation of fractures, voids, and annuli as the grout ages (Walter, et al., 2009).

Theoretically, the reductive capacity of the grout is proportional to the sulfide content of the slag. A relationship between sulfide weight percent and the reductive capacity of grout can be deduced from published information. In particular, both Kaplan, et al. (2005) and Lukens, et al. (2005) have measured a slag reductive capacity of 0.82 meq e⁻ per gram of slag (see Table 1-2). Assuming a sulfide content of 0.77 weight percent based on a chemical analysis of an Idaho National Laboratory slag sample reported by the supplier LaFarge (Waldron, 2007) and a mass fraction of slag in the grout of 0.061, based on the grout formulation for Savannah River Site Tanks 18 and 19 (Kaplan, et al., 2005), the following relationship between the reductive capacity of the grout (R) and the weight percent of sulfide in slag is obtained:

$$R \text{ (meq e}^{-}\text{/g of grout)} = 0.06494 \text{ wt\% sulfide in slag} \quad (4-2)$$

Sensitivity of the grout oxidized fraction to the diffusion coefficient, fracture spacing, and initial reductive capacity, R_0 , is shown in Figure 4-1. Figure 4-1 assumes a sulfide content of 0.1, 0.5,

and 1.0 wt%, respectively. The shaded region in each plot represents the uncertainty envelope (one order of magnitude) associated with the diffusion coefficient, with other parameters being fixed. The envelope is shown for spacing values of 0.1 m, 1.0 m, and 10.0 m in each plot.

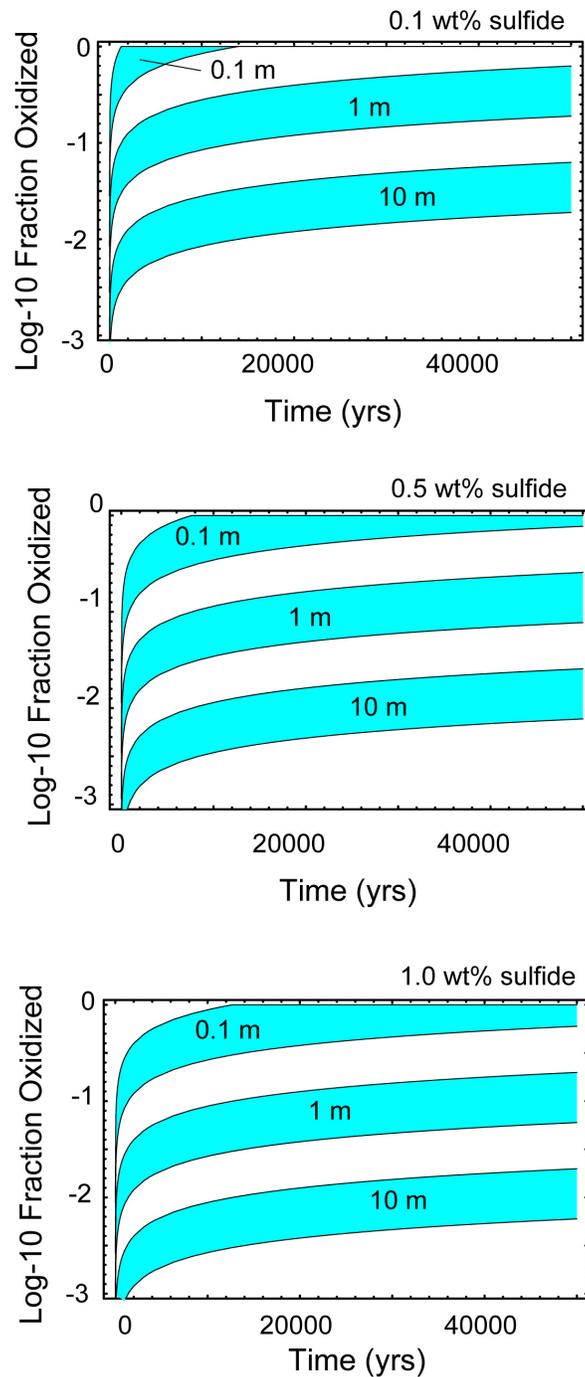


Figure 4-1. Grout Fraction Oxidized (Base-10 Logarithm) Versus Time for Different Combinations of Fracture Spacing and Weight Percent Sulfide in Slag. The Shaded Band for Each Combination of Spacing and Weight Percent Sulfide Represents the Uncertainty Band Associated With the Uncertain Diffusion Coefficient.

5 CONCLUSIONS AND DISCUSSIONS

For a wide range of hydrological conditions, oxygen concentrations in through-going vertical fractures and conduits in subsurface vaults and tanks are expected to be maintained at or near the levels of the surrounding soil by a combination of gas-phase diffusion and liquid-phase advection. This is because of the relatively slow rate of diffusion in the pore space of the intact grout, which becomes the rate-limiting process for oxygen loss to the oxidation reaction. Given the long timeframes of interest in performance assessments, it is concluded that transport processes in the fractures can easily resupply the fractures with oxygen from the surrounding soil.

The finding that diffusion in the pore space of intact grout material is the rate-limiting process for grout oxidation has important practical implications for assessing the longevity of the reducing environment in grouted systems for radioactive waste disposal. Specifically, this finding suggests that detailed process-level models coupling fracture transport processes with matrix diffusion and chemical reactions can be avoided. Simpler models coupling oxygen diffusion and grout oxidation reaction can be used instead, with fractures representing internal boundary conditions with specified oxygen concentrations.

For the idealized situation of parallel fractures in an infinite medium, the fraction of the grout that is oxidized as a function of time may be estimated using the parametric Eq. (4-1). The oxidized fraction of a reducing grout estimated in this way agrees well with the modeling results.

Note that these results presume liquid saturated pores in the grout matrix and also neglect microfractures in the grout. Partial saturation in the grout matrix would lead to larger effective diffusion through gas-phase diffusion. Similarly, microfractures would also enhance the diffusion relative to unfractured grout.

The following analyses are identified as possible future extensions of this work.

- Evaluate the effects of enhanced diffusion due to microfractures or partial liquid saturation in the grout matrix.
- Implement the diffusion/reaction models in commercially available software, such as COMSOL Multiphysics[®] and PetraSim/ToughReact, which would make it feasible to consider detailed representations of fracture and tank/vault geometries in two and three dimensions.
- Extend the parametric Eq. (4-1) to accommodate realistic distributions of fracture spacing.
- Include the simultaneous transport of radionuclides that are mobilized as the grout is oxidized.
- Evaluate the effect of grout carbonation, a process that could slow the oxidation process by reducing grout porosity and inhibiting oxygen transport near fractures.
- Complement the modeling work with laboratory experiments to measure diffusion coefficients and to better understand the ability of slag-bearing grouts to mitigate the release of redox-sensitive radioelements from grouted waste.

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