

## ESTIMATED LONGEVITY OF REDUCING ENVIRONMENT IN GROUTED SYSTEMS FOR RADIOACTIVE WASTE DISPOSAL

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### Introduction

A key factor determining the release and transport of redox-sensitive radioelements (e.g., technetium, selenium) 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. This effect has been ascribed to the release of sulfide species, predominantly as  $S^{2-}$ , into the pore fluid upon hydration of the slag (Atkins and Glasser, 1992), which imposes a strongly reducing redox potential on the system. There is significant uncertainty regarding the long-term persistence of the reducing capabilities of the slag-bearing grout and its long-term effect on radionuclide release and transport. 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—in the gas phase or dissolved in infiltrating water—which could react with the blast furnace slag and decrease the grout reductive capacity.

### Computational Approach

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. 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, 2007) was used. In this approach, the oxidation-reduction reaction is written as an effective reaction that consumes oxygen ( $O_2$ ) and grout-reducing equivalents ( $R$ ) and produces oxidized grout ( $RO_2$ ):



The oxygen conservation equation in the fractures is given by

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

where

- |                           |   |   |
|---------------------------|---|---|
| $\phi_f$                  | — | fracture internal porosity (with a value of 1 for an open fracture containing no sediment)  |
| $S_l$ and $S_g$           | — | liquid and gas saturation in the fracture   |
| $C_l$ and $C_g$           | — | liquid-phase and gas-phase oxygen concentration [meq e <sup>-</sup> /m <sup>3</sup> ]       |
| $\Omega_l$ and $\Omega_g$ | — | liquid-phase and gas-phase fluxes in the fracture [meq e <sup>-</sup> /(m <sup>2</sup> yr)] |

$$\psi_{f \rightarrow m} = \frac{\phi}{b} D_e \left. \frac{\partial C'}{\partial x} \right|_{x=0} \quad \begin{aligned} & \text{fracture-to-matrix oxygen transfer rate [meq e\(^-\)/(m\(^3\) yr)]} \\ t & \text{--- time [yr]} \\ z & \text{--- vertical distance from the surface of the grouted system [m]} \\ b & \text{--- fracture half-aperture [m]} \end{aligned}$$

The oxygen conservation equation in the matrix is given by

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

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

where

$\phi$	—	matrix porosity
$\rho_g$	—	bulk density of the grout [kg/m <sup>3</sup> ]
$D_e$	—	effective diffusion coefficient in the matrix [m <sup>2</sup> /yr]
$C'$	—	oxygen concentration in the matrix pore water [meq e <sup>-</sup> /m <sup>3</sup> ]
$k$	—	grout oxidation rate constant [m <sup>3</sup> /(yr meq e <sup>-</sup> )]
$R$	—	grout reductive capacity [meq e <sup>-</sup> /kg]
$x$	—	coordinate in the direction perpendicular to the fracture [m]

## Results

Oxygen concentrations were calculated versus depth along the fracture at different times for several different combinations of fracture aperture, fracture spacing, and fracture hydraulic conductivity. The modeling cases include both open fractures and wide fractures filled with sediment. The results indicate that for a wide range of hydrological conditions, oxygen concentrations in through-going vertical fractures in grouted subsurface systems for radioactive waste disposal are maintained at or near the levels of the surrounding soil by a combination of gas-phase diffusion and liquid-phase advection. This is because gas-phase oxygen diffusion in the fracture is fast compared with the rates of diffusive loss to the porous grout matrix. In other words, grout oxidation is controlled by the diffusion rate in the grout. For the long time frames 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 within the matrix can be used instead, with fractures representing internal boundary conditions with specified oxygen concentrations. The conference poster will compare the results of these simpler models with those of the numerical model and also present sensitivity analyses to assess the relative importance of the diffusion coefficient, grout reductive capacity, and fracture spacing to rate of grout oxidation.

## Acknowledgment

This abstract was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA<sup>®</sup>) for the U.S. Nuclear Regulatory Commission (NRC) under

Contract No. NRC-02-07-006. The activities reported here were performed on behalf of the NRC Office of Federal and State Materials and Environmental Management Programs, Division of Waste Management and Environmental Protection. This abstract is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

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