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# Nuclear Waste Management Program Summary Report

Workshop on Research and Development Needs in Backfill for Long Term Storage of Nuclear Waste in Deep Geologic Repositories, held at the National Bureau of Standards, Washington, DC, April 13-14, 1981

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## EVALUATION OF BACKFILL AS A BARRIER TO RADIONUCLIDE MIGRATION IN A HIGH LEVEL WASTE REPOSITORY1,2

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### ABSTRACT

The feasibility of using highly sorptive synthetic minerals such as zeolites or titanates as backfill in a HLW repository has been evaluated in terms of the NRC 1,000 yr containment and  $10^{-5}$ /yr controlled release criteria. The results indicate that for groundwater velocities below 1 ft/yr, diffusion and sorption are the dominant processes controlling radionuclide migration in backfill systems. A 3-ft-thick bed of synthetic zeolite backfill can provide total containment of activity released continuously from a 55-gallon glass monolith for a period of up to 1,000 years. For longer time periods of up to  $10^{6}$  years, the controlled release rate of  $10^{-5}$ /yr can be met by a >10-ft-thick bed of zeolite backfill, assuming the glass monolith to be the source term. In the absence of the waste form as an engineered barrier, a bed thickness of 3 to 10 ft is required to

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satisfy the controlled release criterion for a period of up to  $10^5$  years. With a bed thickness of 200 ft, synthetic zeolites can be used as backfill to provide containment of the total U.S. waste inventory ( $10^9$  Ci), if it were placed in one repository, for periods up to  $10^6$  years. Zeolites are known to exhibit radionuclide-specific sorption properties. We believe that the range of sorption coefficients ( $10^3-10^4$  ml/g) considered in the calculations will cover the various zeolite-radionuclides systems. We wish to emphasize that the above estimates are conservative since diffusion occurs radially and we have only considered uni-dimensional transport in our models. In addition, radioactive decay of the nuclides has not been considered in the calculations.

We also wish to note that in this report we have not dealt with radiation and thermal stability of backfill materials. Zeolites have been used to clean radioactivity from water systems and have been loaded to as high as 75,000 curies per MTHM. Although we believe that zeolites should be structurally stable to low radiation loadings (approx. 1,000 curies per cubic foot) and that radiolysis efforts should not be important at these levels of radiation, very little work exists in this area. In addition, we have not addressed the retention of long-lived anionic species such as  $\text{SeO}_{4}^{2-}$ , I-,  $\text{TcO}_{4}^{-}$ . It appears that other materials will have to be added to backfill to maximize its effectiveness for retention of all radionuclides of interest.

### INTRODUCTION

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The operational life of a geologic high level waste (HLW) repository after decommissioning can be divided into two time periods: (a) the period ( $\langle 1,000$ yr) during which the short lived fission products dominate the hazard posed by the waste, and (b) the long term period ( $\geq 1,000$  yr) during which the hazard is dominated by the very long lived isotopes including the actinides [1]. In view of these considerations, the Nuclear Regulatory Commission (NRC) had adopted a strategy for regulatory and licensing the disposal of high level radioactive wastes in geologic repositories which requires that the engineered systems of the underground facility meet the following criteria [2]:

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a. Containment of all radionuclides in HLW for at least the first 1,000 years after decommissioning of the geologic repository, assuming expected events and processes. This containment shall result from properties of the waste package.

- b. Starting 1,000 years after decommissioning of the geologic repository, the radionuclides present in HLW will be released from the engineered system to the geologic setting at an annual rate that in no case greater than one part in one hundred thousand of the total activity present within the underground facility at that time, assuming expected processes and events.
- c. For transuranic waste (TRU), the engineered system shall be designed so that following decommissioning of the geologic repository the annual release rate from the underground facility into the geologic setting is at most one part in one hundred thousand of the total activity present in the underground facility at any time following decommissioning.

Most of the current Department of Energy (DoE) programs in high levels waste research are investigating the waste form and container as potential components of a waste package in meeting the containment requirements outlined above. In this report, we have attempted to evaluate the effectiveness of using synthetic zeolites and titanates as potential backfill materials in an HLW repository. It should be pointed out that a DoE waste package is defined to include everything that is placed in the waste repository emplacement hole, i.e., the waste form, filled container, overpack, sleeve, and backfill. The NRC waste package includes discrete backfill [3] in contrast to non-discrete backfill in DoE definition. Since the 1,000 yr criterion applies specifically to the waste package and the  $10^{-5}$ /yr controlled release criterion refers to the engineered system, we have evaluated the effectiveness of backfill in meeting both performance requirements: discrete backfill for 1,000 yr containment and non-discrete backfill for controlled release.

### Zeolites and Titanates as Backfill

Although backfill in an HLW repository has been identified to provide several functions, the most important role is to retard migration of radionuclides in groundwater that has reached the waste in the event of a container breach. It is primarily this property that we have considered in our evaluation of synthet zeolites and titanates for backfill. In addition to providing a high potential for required retention of radionuclides, synthetic backfill materials of regularly shaped small spheres can be used, through prior selection of the mass, volume, shape, and packing densities, to predetermine and control the groundwater flow rates and patterns into and through the engineered underground facility for varying aquifer pressures and flow rates. Such a modification of the hydrodynamics of an engineered facility could be advantageous in that rapid radionuclide transport by advection would be minimized, resulting in diffusioncontrolled transport.

Existing technology, widely used in purification systems for water reactors, has demonstrated that synthetic materials including a wide range of zeolites can be used to quantitatively hold up fission products and actinides. A most prominent example of zeolite application to waste management is the use of IONSIV-IE95 and Zeolon 900 in the Submerged Demineralized System (SDS) to be used to decontaminate water from the Three Mile Island Unit 2 Nuclear Power Plant [4]. Another such example is the storage of krypton-85 in sodalite zeolite [5]. Recently, Nowak [6] and Winslow [7] at Sandia Laboratories and Komarneni and Roy [8] at Pennsylvania State University have examined the sorption properties of zeolites as potential backfill material for use in a HLW repository. Pennsylvania State University is also investigating the use of mixtures of zeolites and clay minerals for backfill material around a waste package and the fixation properties of sorbed radionuclides of various zeolite minerals [9].

Sodium titanate materials have been developed at Sandia Laboratories for quantitative removal of fission products and actinides from commercial liquid wastes [10, 11]. Subsequent pressure sintering of the loaded material results in a dense ceramic waste form resistant to leaching. Based on the high decontamination factors observed in HLW studies, the Sandia titanate materials are also being investigated for the decontamination of defense liquid wastes stored at the Hanford site in Washington.

In this report, we have attempted to evaluate the feasibility of using highly sorptive materials such as synthetic zeolites and titanates as backfill in a HLW repository. The effectiveness of such a barrier with respect to radionuclide retention has been assessed in terms of the NRC release criteria discussed above.

Radionuclide Transport Processes

To evaluate the migration of radionuclides in an ion exchange backfill barrier, we have to first consider the dominate transport mechanisms. The principal mechanisms controlling the nature and extent of radionuclide transport in sorptive materials are ion exchange, sorption, diffusion, precipitation, advection, and other irreversible reactions. Ion exchange and sorption processes are essentially reversible (at least over short time periods), resulting in a net retardation in the diffusion-controlled ion migration. The extent of retardation will be primarily determined by the sorption kinetics and equilibria of solid-fluid interactions. Non-reactive ions such as tritium, however, do not exhibit interactions with particle surfaces. In this case, ion exchange and sorption processes are not significant and, consequently, the migration is primarily controlled by diffusion and advection.

Precipitation of dissolved radionuclides as authigenic minerals will decrease the rate of radionuclide migration. Formation of new minerals, immobilizing radionuclides release from the waste form, as a result of quaternary interactions involving waste/backfill/host rock with hydrothermal fluids has been documented [12]. However, such data are not available for the various backfill materials. Therefore, precipitation, as a retardation process, will not be considered in this report.

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Similarly, irreversible reactions such as fixation of sorbed ions with aging of the sorbent can also decrease the rate of radionuclide migration. Recently, it was reported that synthetic zeolites, used for decontamination purposes at Hanford, were found to fix certain radionuclides irreversibly in a period of less than five years [13]. Although this mechanism could be potentially effective in retarding radionuclides in a bed of synthetic zeolites, the available data are insufficient at this time for this mechanism to be considered in our transport model.

At a recent Waste Rock Interaction Technology Meeting in Seattle, a paper was presented describing the role of fine suspended particulates in transporting radionuclides [14]. This process could serve as a potentially important mechanism for radionuclide migration in argillaceous backfill materials which commonly contain extremely small particulates. However, in the case of synthetic materials, the particle size distribution would be very narrow, giving rise to a relatively uniform particle size. Therefore, we believe that this mechanism will not contribute significantly to an increase in the rate of radionuclide migration in backfill systems. However, the significance of this process as a transport mechanism for radionuclides should be investigated.

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The principal transport mechanisms which we have considered for evaluating zeolite backfill are diffusion, sorption, and advection. Since groundwater flow rate is relatively low in a realistic repository situation, dispersion associated with advection is considered to be negligible. An example of radionuclide transport by advection, diffusion, and a combination of advection, diffusion, and sorption processes is displayed in figure 1 [15]. As shown in figure 1, pure diffusion corresponds to radionuclide migration as a result of interstitial concentration gradient for non-reactive ions such as tritium. For reactive ions such as  $Cs^+$  and  $Sr^{2+}$  and assuming bulk fluid flow to be negligible, the transport is primarily determined by diffusion and sorption, where the sorption equilibrium coefficient determines the extent of ion retardation as compared with diffusional transport for non-reactive ions. For systems having a high groundwater flow velocity, advection becomes the dominant transport process as compared with diffusion (figure 1). Dispersion effects, resulting from the variation in bulk fluid flow velocities between the particles, could give rise to a broadening of the advective front.

#### MODEL CALCULATIONS

We have developed one-dimensional models that describe quantitatively the transport of radionuclides in a backfill bed. A range of values are considered for groundwater flow rate, sorption coefficient, bed thickness, and transit time.

Phenomenological Model 1

In model 1, the details of which are given in appendix 1, we have assumed a waste glass, having a constant leach rate over a longer period of time, to be the source term. A constant concentration is maintained at x=0, the interface between the waste glass and backfill. In other words, it is assumed that the radionuclide source is non-depleting, time invariant. The transport mechanisms considered are diffusion, sorption, and advection. The groundwater velocity is assumed to be constant with time and uniform throughout the bed. The dispersion term, resulting from localized velocity variations around the particles, is assumed to be negligible. Finally, radioactive decay of the source term and precipitation and fixation of the radionuclide are not considered.

Nowak [6] simplified a material balance equation around a differential volume element in the backfill bed. His formulation is directly applicable to the present analysis. It consists of a linear partial differential equation with three terms: (1) the rates of accumulation (or depletion) of sorbing species in the liquid and on the solid, (2) the net transport of liquid phase species by advection, and (3) the net transport of liquid phase species by ion diffusion. The groundwater flow in a repository must be considered and could serve as a potentially important transport process, especially for non-reactive radionuclides.

Using model 1, the results were calculated for a range of conditions and the concentration-bed thickness profiles for various transit times are displayed in

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figure 2. In figure 2(a), for a sorption coefficient of 1,000 ml/g and a water velocity of 1 ft/yr, the 1,000 year and 10,000 year profiles show that for relatively short time periods diffusion plus sorption are the rate controlling processes, with the initial concentration dropping by a factor of >10<sup>6</sup> within 20 feet of backfill thickness. However, for longer time periods of up to 100,000 years and greater, transport associated with bulk fluid flow becomes dominant, even for reactive ions having a sorption coefficient of 1,000 ml/g. In the absence of bulk fluid flow, the advective term becomes zero. As shown in figure 2(b), the transport is dominated by diffusion and sorption. These findings are in general agreement with those reported recently by Nowak [21]. For materials having negligible sorptive capacity such as quartz, and in a zero groundwater flow stationary system, radionuclide transport is determined by pure diffusion via interstitial water (figure 2(c)), emphasizing the importance of sorption as a retardation process in the transport of radionuclides through a backfill barrier.

### Phenomenological Model 2

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In this model, we exclude the waste form as an engineered barrier which maintained constant concentration at the interface of the glass and backfill by continuous congruent leaching over a period of time. Instead, at zero time (t=0), the total concentration of the radioactive waste is hypothesized to enter into the backfill instantaneously along the x direction as a sharp step increase (more precisely as a delta function) in its liquid phase concentration c from zero to a constant value  $C_0$ . We derived a mathematical expression using the appropriate initial and boundary conditions in appendix 2. The calculated results were obtained using the same range of parameters given in table 1. The assumption of an instantaneous pulse at time t=0 and continuously depleting over a period of time for the source term in model 2 means that no reliance is placed on the waste form as an engineered barrier. Concentration-bed thickness profiles for various transit times, based on model 2 using the parameters given in table 1, are given in figure 3.

### Evaluation of NRC Criteria

Although the concentration-bed thickness profiles generated using models 1 and 2 (figure 2 and 3) are useful in terms of identifying the processes that control radionuclide migration in a sorptive backfill system and in determining their relative magnitudes, quantitative information is required to address the performance objectives set by NRC. For this purpose, we assumed the source term to be a glass monolith having a volume of 55 gallons. Assuming 30 percent waste loading in the glass, an activity of approximately 4.2 Ci/cm<sup>3</sup> of glass monolith is calculated. The age of the waste is assumed to be approximately 1.5 years old [21]. The average glass leach rate is considered to be  $10^{-3}$  g/cm<sup>2</sup>-yr.

Based on assumed leach rates for the waste glass, surface areas of the glass monolith and the total amounts of radioactivity released from the source for the periods  $10^3$  and  $10^6$  years as estimated from the profiles shown in figure 2, we estimated the total amount released from a 3-ft-thick backfill, having a range of sorptive capacities, in a period of 1,000 years at the groundwater flow velocity of 1 ft/yr. As shown in table 2, a 3-ft-thick bed of backfill materials, such as zeolites having a sorption coefficient of 10<sup>4</sup> ml/g, will contain practically all the inventory released from the waste for a period of up to 1,000 years. This implies that a discrete zeolite backfill will satisfy the NRC 1,000 year containment criterion. Table 3 shows calculated results of fractional controlled release rate from a 10- and a 100-ft-thick backfill bed over a period  $10^6$  years. In these calculations, the assumptions made for the source term and backfill are the same as those described in table 2. Assuming a leach rate of less than  $10^{-3}$  g/cm<sup>2</sup>-yr and a surface area of the glass monolith to be 3.6 x  $10^4$  cm<sup>2</sup>, the NRC controlled release criteria can be met using a >10-ftthick non-discrete zeolite backfill bed for periods of up to 10<sup>5</sup> years. These calculations show the significance of a waste form having a low leach rate with respect to meeting the controlled release criterion. In such a situation, the sole purpose of the backfill would be to control water ingress in order to minimize the probability of container corrosion. It must be emphasized that bulk fluid flow, based on a groundwater velocity of 1 ft/yr, also contributes

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to radionuclide transport. In a realistic repository situation, the flow velocities are much smaller than that assumed in our calculations. In that case, the transport would be predominantly diffusion-controlled, resulting in a more effective containment by the backfill barrier.

Using model 2 and making the same assumptions for the source term and backfill barrier, we obtained estimates of the total amount of activity released from a 3-ft-thick backfill barrier in a period of  $10^3$  years. As shown in table 4, the calculated values indicate that the 1,000 year containment criterion will be met by a 3-ft-thick bed of backfill with sorption coefficients in the range of  $10^4$  ml/g. Also included in table 4 are values for fractional amounts of activity released from the backfill barrier in 1,000 years.

Using the same model and considering a time period of  $10^5$  years and bed thicknesses of 3 ft and 10 ft, we obtained estimates of fractional release per year from the backfill bed (table 5). The results show that for backfill materials having sorption coefficients in the range of  $10^4$  ml/g, the annual fractional release from 3-ft-and 10-ft-thick beds are  $10^{-5}/yr$  and  $10^{-6}/yr$ , respectively. This indicates that the controlled release criterion of  $10^{-5}/yr$  will be met by highly sorptive backfill materials such as synthetic zeolites and/or titanates for long period of time.

Model Calculation for Total U.S. Waste Inventory

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In order to demonstrate the effectiveness of backfill as a barrier to radionuclide migration, we assumed the source term to be the total U.S. waste inventory and calculated the total thickness of backfill that would be required to provide controlled release rate over a period of 10<sup>6</sup> years.

Using models 1 and 2, we used a value of  $10^9$  Ci [23] for the total waste inventory in the U.S. [12] and 100- and 200-ft for bed thicknesses. The calculated estimates of radionuclide release are compiled in tables 6 and 7. Table 6, based on model 1, shows that the annual release from 200-ft-thick backfill, having a sorption coefficient of  $10^4$  ml/g, is on the order of  $10^{-80}$  Ci/yr. This indicates that the total containment will be achieved during this period. Table 7, based on model 2, also shows that a 200-ft-thick bed of backfill  $(K_d = 10^4 \text{ ml/g})$  will provide total containment. A bed thickness of 100 ft, however, is not sufficient to obtain the desired containment.

#### CONCLUSIONS

For groundwater velocities below 1 ft/yr, diffusion and sorption are the dominant processes controlling radionuclide migration in highly sorptive backfill materials such as synthetic zeolites. A 3-ft-thick bed of synthetic zeolite backfill can provide total containment of activity released continuously from a 55-gallon glass monolith for a period of up to 1,000 years. For longer time periods of up to  $10^6$  years, the controlled release rate of  $10^{-5}/yr$  can be met by a >10-ft-thick bed of zeolite backfill, assuming the glass monolith to be the source term. In the absence of the waste form as an engineered barrier, a bed thickness of 3 to 10 ft is required to satisfy the controlled release criterion for a period of up to  $10^5$  years. With a bed thickness of 200 ft, synthetic zeolites can be used as backfill to provide containment of total U.S. waste inventory ( $10^9$  Ci), if it were placed in one repository, for periods of up to  $10^6$  years.

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Parameters Considered in Radionuclide Transport Calculations

Backfill Bed Thickness (ft): 1, 3, 10, 100 Transit Time (years): 1,000, 10,000, 100,000, 1,000,000 Sorption Coefficient (ml/g): 1, 10, 100, 1,00, 10,000 Ion Diffusion Coefficient (cm<sup>2</sup>/sec)[6]: 10<sup>-5</sup> Groundwater Velocity (ft/yr)[16,17,18]: 0, 1 Bed Porosity[19]: 0.34 Bed Density (g/cm<sup>3</sup>)[20]: 0.423

## Total Release of Radioactivity from a 3-ft-thick Backfill in 10<sup>3</sup> Years (Model 1)

Total Assumed Released from Backfill (Ci)		
$SA = 3.6 \times 10^4 (cm^2)$	$SA = 3.6 \times 10^6 (cm^2)$	
$4 \times 10^4$	4 x 106a	
$4 \times 10^{0}$	$4 \times 10^2$	
$5 \times 10^{-46}$	$5 \times 10^{-44}$	
	Total Assumed Release $SA = 3.6 \times 10^4 (cm^2)$ $4 \times 10^4$ $4 \times 10^0$ $5 \times 10^{-46}$	

a Artificial number indicating total inventory release.

 $V_g = 1$  ft/yr; backfill thickness = 3 ft; leach rate (LR) =  $10^{-3}$  g/cm<sup>2</sup>-yr;

 $C_0 = LR \times SA \times transit time/area under the concentration curves;$ 

SA = surface area of the glass monolith.

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### Table 3

Fractional Release Rate from a 10-ft-and a 100-ft-Thick Backfill in 10<sup>6</sup> Years (Model 1)

		Fractional	Release Rat	e From Backf	ill (/yr)
Backfill	Sorption Coefficient	SA = 3.6	$x 10^4 (cm^2)$	SA = 3.6	$x  10^{6} (cm^{2})$
	Kd (m1/g)	10-ft	100-ft	<u>10-ft</u>	100-ft
	100	6.8 x 10 <sup>-5</sup>	6.7 x 10 <sup>-5</sup>	6.8 x 10-3	6.7 x 10 <sup>-3</sup>
	1,000	6.7 x 10 <sup>-5</sup>	$6.0 \times 10^{-5}$	6.7 x $10^{-3}$	$6.0 \times 10^{-3}$
	10,000	$6.0 \times 10^{-5}$	$3.6 \times 10^{-9}$	$6.0 \times 10^{-3}$	$3.6 \times 10^{-7}$

 $V_g = 1$  ft/yr; leach rate (LR) =  $10^{-3}$  g/cm<sup>2</sup>-yr;

SA = surface area of the glass monolith.

# Fractional and Total Release from a 3-ft-Thick Backfill in 10<sup>3</sup> Years (Model 2)

Backfill Sorption Coefficient

Kd (ml/g)	Fractional Release	Total Release (Ci)
100	9.97 x 10-1	8.80 x 10 <sup>5</sup>
1,000	$3.25 \times 10^{-4}$	$2.90 \times 10^2$
10,000	5.93 x 10 <sup>-50</sup>	5.20 x $10^{-44}$

 $V_g = 1 \text{ ft/yr}$ , backfill thickness = 3 ft.

## Table 5

Fractional Release Rate from a 3-ft-Thick Backfill and a 10-ft-Thick Backfill in 10<sup>5</sup> Years (Model 2)

Backfill Sorption Coefficient	Fractional Release Per Year (/yr		
Kd (m1/g)	3-ft	10-ft	
100	>10-5	. >10-5	
1,000	>10-5	>10-5	
10,000	9.97 x 10-6	1.85 x 10-6	

 $V_g = 1 ft/yr.$ 

Annual Release From a 200-ft-Thick Backfill for 10<sup>6</sup> Years, Assuming the Source of Term to be Total U.S. HLW Inventory (Model 1)

Backfill Sorption Coefficient	Annual Release From Backfill (Ci/yr)	
Kd (ml/g)	$SA = 2.4 \times 10^5 (cm^2)$	$SA = 2.4 \times 10^7 (cm^2)$
100	4 x 102	4 x 104
1,000	3 x 10 <sup>2</sup>	3 x 10 <sup>4</sup>
10,000	$3 \times 10^{-80}$	3 x 10 <sup>-78</sup>

 $V_g = 1$  ft/yr; backfill thickness = 200 ft; leach rate (LR) =  $10^{-3}$  g/cm<sup>2</sup> yr; SA = surface area of all the glass monolith considered.

## Table 7

Annual Release From a 200-ft-Thick Backfill for 10<sup>6</sup> Years, Assuming the Source Term to be Total U.S. HLW Inventory (Model 2)

Backfill Sorption Coefficient	Annual Release From Backfill
Kd (ml/g)	(Ci/yr)
100	103
1,000	103
10,000	10-79
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10,000	10-79

 $V_g = 1 \text{ ft/yr}$ .

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Figure 2. Concentration vs. bed thickness profiles for various transit times based on model 1: (a)  $K_d = 1000 \text{ ml/g}$ ,  $V_g = 1 \text{ ft/yr}$ ; (b)  $k_d = 1000 \text{ ml/g}$ ,  $V_g = 0 \text{ ft/yr}$ ; (c)  $k_d = 1 \text{ ml/g}$ ,  $V_g = 0 \text{ ft/yr}$ ;  $A = 10^3 \text{ yr}$ , B = 104 yr, C = 105 yr, D = 106 yr



Figure 3. Concentration vs. bed thickness profiles for various transit times based on model 2: (a)  $K_d = 1000 \text{ ml/g}$ ,  $V_g = 0 \text{ ft/yr}$ ; (b)  $k_d = 100 \text{ ml/yr}$ ,  $V_g = 1 \text{ ft/yr}$ ;  $A = 10^3 \text{ yr}$ ,  $B = 10^4 \text{ yr}$ ,  $C = 10^5$ ,  $D = 10^6 \text{ yr}$ 

### APPENDIX 1

The simplified equation of the differential mass balance is

$$\frac{\delta c(x,t)}{\delta t} + \frac{V_g}{R_f} \frac{\delta c(x,t)}{\delta x} - \frac{D_f}{\sqrt{2} R_f} \frac{\delta^2 c(x,t)}{\delta x^2} = 0 \qquad (1)$$

where

$$R_{f} = (1 + \frac{\rho_{d} K_{d}}{\epsilon})$$
, the retardation factor

x = the distance from the interface of the glass and the zeolite along the direction of flow and longitudinal diffusion

t = time

- c(x,t) = liquid phase concentration, quantity of sorbing species per unit volume of liquid at distance along flow direction x and time t
  - ε = effective porosity of bed (fraction of bed volume containing flowing liquid)

 $V_g$  = average interstitial velocity of flowing water

- $D_f/\sqrt{2}$  = coefficient of longitudinal fluid diffusion with a tortuosity factor to account for the tortuous diffusion path through the porous bed
  - $\rho_b$  = the bulk packing density of solid sorbent, mass of solid per unit bed volume
  - Kd = the distribution coefficient for a linear sorption isotherm. The ratio of quantity of sorbed species per unit mass of solids to quantity of mobile species in the liquid phase per unit volume of liquid.

The boundary condition is

$$c(x = 0, t > 0) = C_0$$

The initial condition is

$$c(x > 0, t = 0) = 0.$$

Define

$$U(x,t) = c(x,t) \cdot \exp\left[\frac{-V_{g,x}}{\sqrt{2} D_{f}}\right] \cdot \exp\left[\frac{V_{g}^{2} \cdot t}{2\sqrt{2} \cdot D_{f} \cdot R_{f}}\right]$$

Then, Equation (1) is reduced to a heat equation of U(x,t) as function of x and t. With the rearrangement of boundary and initial conditions, the Fourier transform is applied to the heat equation, and the subsequent convolution gives the following solution

$$c(x,t)/C_{o} = 1 - \frac{1}{2} \left[ \operatorname{erfc} \left\{ \frac{v_{g} \cdot \sqrt{t}}{2^{3/4} \sqrt{D_{f} \cdot R_{f}}} - \frac{\sqrt{R_{f}} \cdot x}{2^{3/4} \sqrt{D_{f}} \cdot t} \right\} - \exp \left\{ \frac{\sqrt{2} v_{g} \cdot x}{D_{f}} \right\} \cdot \operatorname{erfc} \left\{ \frac{v_{g} \cdot \sqrt{t}}{2^{3/4} \sqrt{D_{f}} \cdot R_{f}} + \frac{\sqrt{R_{f}} \cdot x}{2^{3/4} \sqrt{D_{f}} \cdot t} \right\} \right]$$
(2)

where

erfc(y) = 1 - erf(y) and erf(y) is the error function of y.

The integration from x = backfill thickness to infinity is done numerically for the total release from backfill.

### APPENDIX 2

The same differential equation is used as in model 1. The new constraint instead of the boundary condition is

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 $\int_{-\infty}^{\infty} C(x>0, t>0) dx = C_{total}$ 

and the new initial condition is

 $C(x > 0, t = 0) = C_{total} \delta(x)$ 

where  $\delta(x)$  is a delta function of x and  $C_{total}$  is a total quantity of sorbing species.

The transformation technique may not be plausible in this case for the closed form solution. However, since we know the response of step function from appendix 1, the response of the delta function should be the derivative of the response of the step function with respect to x: the derivative of equation (2) of appendix 1. Further, we need the integral from x equals the backfill thickness of infinity, which is equivalent to the response function of appendix 1 (equation 2).



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# Nuclear Waste Management Program

Summary Report

# MBS April publicationi

# Nuclear Waste Management Program Summary Report

Workshop on Research and Development Needs in Backfill for Long Term Storage of Nuclear Waste in Deep Geologic Repositories, held at the National Bureau of Standards, Washington, DC, April 13-14, 1981

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## EVALUATION OF BACKFILL AS A BARRIER TO RADIONUCLIDE MIGRATION IN A HIGH LEVEL WASTE REPOSITORY1,2

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ABSTRACT

The feasibility of using highly sorptive synthetic minerals such as zeolites or titanates as backfill in a HLW repository has been evaluated in terms of the NRC 1,000 yr containment and  $10^{-5}$ /yr controlled release criteria. The results indicate that for groundwater velocities below 1 ft/yr, diffusion and sorption are the dominant processes controlling radionuclide migration in backfill systems. A 3-ft-thick bed of synthetic zeolite backfill can provide total containment of activity released continuously from a 55-gallon glass monolith for a period of up to 1,000 years. For longer time periods of up to  $10^{6}$  years, the controlled release rate of  $10^{-5}$ /yr can be met by a >10-ft-thick bed of zeolite backfill, assuming the glass monolith to be the source term. In the absence of the waste form as an engineered barrier, a bed thickness of 3 to 10 ft is required to

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satisfy the controlled release criterion for a period of up to  $10^5$  years. With a bed thickness of 200 ft, synthetic zeolites can be used as backfill to provide containment of the total U.S. waste inventory ( $10^9$  Ci), if it were placed in one repository, for periods up to  $10^6$  years. Zeolites are known to exhibit radionuclide-specific sorption properties. We believe that the range of sorption coefficients ( $10^3-10^4$  ml/g) considered in the calculations will cover the various zeolite-radionuclides systems. We wish to emphasize that the above estimates are conservative since diffusion occurs radially and we have only considered uni-dimensional transport in our models. In addition, radioactive decay of the nuclides has not been considered in the calculations.

We also wish to note that in this report we have not dealt with radiation and thermal stability of backfill materials. Zeolites have been used to clean radioactivity from water systems and have been loaded to as high as 75,000 curies per MTHM. Although we believe that zeolites should be structurally stable to low radiation loadings (approx. 1,000 curies per cubic foot) and that radiolysis efforts should not be important at these levels of radiation, very little work exists in this area. In addition, we have not addressed the retention of long-lived anionic species such as  $\text{SeO}_{4}^{2-}$ , I-,  $\text{TcO}_{4}^{-}$ . It appears that other materials will have to be added to backfill to maximize its effectiveness for retention of all radionuclides of interest.

### INTRODUCTION

The operational life of a geologic high level waste (HLW) repository after decommissioning can be divided into two time periods: (a) the period ( $\langle 1,000$ yr) during which the short lived fission products dominate the hazard posed by the waste, and (b) the long term period ( $\geq 1,000$  yr) during which the hazard is dominated by the very long lived isotopes including the actinides [1]. In view of these considerations, the Nuclear Regulatory Commission (NRC) had adopted a strategy for regulatory and licensing the disposal of high level radioactive wastes in geologic repositories which requires that the engineered systems of the underground facility meet the following criteria [2]:

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- a. Containment of all radionuclides in HLW for at least the first 1,000 years after decommissioning of the geologic repository, assuming expected events and processes. This containment shall result from properties of the waste package.
- b. Starting 1,000 years after decommissioning of the geologic repository, the radionuclides present in HLW will be released from the engineered system to the geologic setting at an annual rate that in no case greater than one part in one hundred thousand of the total activity present within the underground facility at that time, assuming expected processes and events.
- c. For transuranic waste (TRU), the engineered system shall be designed so that following decommissioning of the geologic repository the annual release rate from the underground facility into the geologic setting is at most one part in one hundred thousand of the total activity present in the underground facility at any time following decommissioning.

Most of the current Department of Energy (DoE) programs in high levels waste research are investigating the waste form and container as potential components of a waste package in meeting the containment requirements outlined above. In this report, we have attempted to evaluate the effectiveness of using synthetic zeolites and titanates as potential backfill materials in an HLW repository. It should be pointed out that a DoE waste package is defined to include everything that is placed in the waste repository emplacement hole, i.e., the waste form, filled container, overpack, sleeve, and backfill. The NRC waste package includes discrete backfill [3] in contrast to non-discrete backfill in DoE definition. Since the 1,000 yr criterion applies specifically to the waste package and the  $10^{-5}$ /yr controlled release criterion refers to the engineered system, we have evaluated the effectiveness of backfill in meeting both performance requirements: discrete backfill for 1,000 yr containment and non-discrete backfill for controlled release.

ת au Zeolites and Titanates as Backfill

Although backfill in an HLW repository has been identified to provide several functions, the most important role is to retard migration of radionuclides in groundwater that has reached the waste in the event of a container breach. It is primarily this property that we have considered in our evaluation of syntheti zeolites and titanates for backfill. In addition to providing a high potential for required retention of radionuclides, synthetic backfill materials of regularly shaped small spheres can be used, through prior selection of the mass, volume, shape, and packing densities, to predetermine and control the groundwater flow rates and patterns into and through the engineered underground facility for varying aquifer pressures and flow rates. Such a modification of the hydrodynamics of an engineered facility could be advantageous in that rapid radionuclide transport by advection would be minimized, resulting in diffusioncontrolled transport.

Existing technology, widely used in purification systems for water reactors, has demonstrated that synthetic materials including a wide range of zeolites can be used to quantitatively hold up fission products and actinides. A most prominent example of zeolite application to waste management is the use of IONSIV-IE95 and Zeolon 900 in the Submerged Demineralized System (SDS) to be used to decontaminate water from the Three Mile Island Unit 2 Nuclear Power Plant [4]. Another such example is the storage of krypton-85 in sodalite zeolite [5]. Recently, Nowak [6] and Winslow [7] at Sandia Laboratories and Komarneni and Roy [8] at Pennsylvania State University have examined the sorption properties of zeolites as potential backfill material for use in a HLW repository. Pennsylvania State University is also investigating the use of mixtures of zeolites and clay minerals for backfill material around a waste package and the fixation properties of sorbed radionuclides of various zeolite minerals [9].

Sodium titanate materials have been developed at Sandia Laboratories for quantitative removal of fission products and actinides from commercial liquid wastes [10, 11]. Subsequent pressure sintering of the loaded material results in a dense ceramic waste form resistant to leaching. Based on the high decontamination factors observed in HLW studies, the Sandia titanate materials are also being investigated for the decontamination of defense liquid wastes stored at the Hanford site in Washington.

In this report, we have attempted to evaluate the feasibility of using highly sorptive materials such as synthetic zeolites and titanates as backfill in a HLW repository. The effectiveness of such a barrier with respect to radionuclide retention has been assessed in terms of the NRC release criteria discussed above.

Radionuclide Transport Processes

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To evaluate the migration of radionuclides in an ion exchange backfill barrier, we have to first consider the dominate transport mechanisms. The principal mechanisms controlling the nature and extent of radionuclide transport in sorptive materials are ion exchange, sorption, diffusion, precipitation, advection, and other irreversible reactions. Ion exchange and sorption processes are essentially reversible (at least over short time periods), resulting in a net retardation in the diffusion-controlled ion migration. The extent of retardation will be primarily determined by the sorption kinetics and equilibria of solid-fluid interactions. Non-reactive ions such as tritium, however, do not exhibit interactions with particle surfaces. In this case, ion exchange and sorption processes are not significant and, consequently, the migration is primarily controlled by diffusion and advection.

Precipitation of dissolved radionuclides as authigenic minerals will decrease the rate of radionuclide migration. Formation of new minerals, immobilizing radionuclides release from the waste form, as a result of quaternary interactions involving waste/backfill/host rock with hydrothermal fluids has been documented [12]. However, such data are not available for the various backfill materials. Therefore, precipitation, as a retardation process, will not be considered in this report. Similarly, irreversible reactions such as fixation of sorbed ions with aging of the sorbent can also decrease the rate of radionuclide migration. Recently, it was reported that synthetic zeolites, used for decontamination purposes at Hanford, were found to fix certain radionuclides irreversibly in a period of less than five years [13]. Although this mechanism could be potentially effective in retarding radionuclides in a bed of synthetic zeolites, the available data are insufficient at this time for this mechanism to be considered in our transport model.

At a recent Waste Rock Interaction Technology Meeting in Seattle, a paper was presented describing the role of fine suspended particulates in transporting radionuclides [14]. This process could serve as a potentially important mechanism for radionuclide migration in argillaceous backfill materials which commonly contain extremely small particulates. However, in the case of synthetic materials, the particle size distribution would be very narrow, giving rise to a relatively uniform particle size. Therefore, we believe that this mechanism will not contribute significantly to an increase in the rate of radionuclide migration in backfill systems. However, the significance of this process as a transport mechanism for radionuclides should be investigated.

The principal transport mechanisms which we have considered for evaluating zeolite backfill are diffusion, sorption, and advection. Since groundwater flow rate is relatively low in a realistic repository situation, dispersion associated with advection is considered to be negligible. An example of radionuclide transport by advection, diffusion, and a combination of advection, diffusion, and sorption processes is displayed in figure 1 [15]. As shown in figure 1, pure diffusion corresponds to radionuclide migration as a result of interstitial concentration gradient for non-reactive ions such as tritium. For reactive ions such as  $Cs^+$  and  $Sr^{2+}$  and assuming bulk fluid flow to be negligible, the transport is primarily determined by diffusion and sorption, where the sorption equilibrium coefficient determines the extent of ion retardation as compared with diffusional transport for non-reactive ions. For systems having a high groundwater flow velocity, advection becomes the dominant transport process as compared with diffusion (figure 1). Dispersion effects, resulting from the variation in bulk fluid flow velocities between the particles, could give rise to a broadening of the advective front.

### MODEL CALCULATIONS

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We have developed one-dimensional models that describe quantitatively the transport of radionuclides in a backfill bed. A range of values are considered for groundwater flow rate, sorption coefficient, bed thickness, and transit time.

Phenomenological Model 1

In model 1, the details of which are given in appendix 1, we have assumed a waste glass, having a constant leach rate over a longer period of time, to be the source term. A constant concentration is maintained at x=0, the interface between the waste glass and backfill. In other words, it is assumed that the radionuclide source is non-depleting, time invariant. The transport mechanisms considered are diffusion, sorption, and advection. The groundwater velocity is assumed to be constant with time and uniform throughout the bed. The dispersion term, resulting from localized velocity variations around the particles, is assumed to be negligible. Finally, radioactive decay of the source term and precipitation and fixation of the radionuclide are not considered.

Nowak [6] simplified a material balance equation around a differential volume element in the backfill bed. His formulation is directly applicable to the present analysis. It consists of a linear partial differential equation with three terms: (1) the rates of accumulation (or depletion) of sorbing species in the liquid and on the solid, (2) the net transport of liquid phase species by advection, and (3) the net transport of liquid phase species by ion diffusion. The groundwater flow in a repository must be considered and could serve as a potentially important transport process, especially for non-reactive radionuclides.

Using model 1, the results were calculated for a range of conditions and the concentration-bed thickness profiles for various transit times are displayed in

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figure 2. In figure 2(a), for a sorption coefficient of 1,000 ml/g and a water velocity of 1 ft/yr, the 1,000 year and 10,000 year profiles show that for relatively short time periods diffusion plus sorption are the rate controlling processes, with the initial concentration dropping by a factor of >10<sup>6</sup> within 20 feet of backfill thickness. However, for longer time periods of up to 100,000 years and greater, transport associated with bulk fluid flow becomes dominant, even for reactive ions having a sorption coefficient of 1,000 ml/g. In the absence of bulk fluid flow, the advective term becomes zero. As shown in figure 2(b), the transport is dominated by diffusion and sorption. These findings are in general agreement with those reported recently by Nowak [21]. For materials having negligible sorptive capacity such as quartz, and in a zero groundwater flow stationary system, radionuclide transport is determined by pure diffusion via interstitial water (figure 2(c)), emphasizing the importance of sorption as a retardation process in the transport of radionuclides through a backfill barrier.

### Phenomenological Model 2

In this model, we exclude the waste form as an engineered barrier which maintained constant concentration at the interface of the glass and backfill by continuous congruent leaching over a period of time. Instead, at zero time (t=0), the total concentration of the radioactive waste is hypothesized to enter into the backfill instantaneously along the x direction as a sharp step increase (more precisely as a delta function) in its liquid phase concentration c from zero to a constant value  $C_0$ . We derived a mathematical expression using the appropriate initial and boundary conditions in appendix 2. The calculated results were obtained using the same range of parameters given in table 1. The assumption of an instantaneous pulse at time t=0 and continuously depleting over a period of time for the source term in model 2 means that no reliance is placed on the waste form as an engineered barrier. Concentration-bed thickness profiles for various transit times, based on model 2 using the parameters given in table 1, are given in figure 3.

### Evaluation of NRC Criteria

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Although the concentration-bed thickness profiles generated using models 1 and 2 (figure 2 and 3) are useful in terms of identifying the processes that control radionuclide migration in a sorptive backfill system and in determining their relative magnitudes, quantitative information is required to address the performance objectives set by NRC. For this purpose, we assumed the source term to be a glass monolith having a volume of 55 gallons. Assuming 30 percent waste loading in the glass, an activity of approximately  $4.2 \text{ Ci/cm}^3$  of glass monolith is calculated. The age of the waste is assumed to be approximately 1.5 years old [21]. The average glass leach rate is considered to be  $10^{-3} \text{ g/cm}^2\text{-yr}$ .

Based on assumed leach rates for the waste glass, surface areas of the glass monolith and the total amounts of radioactivity released from the source for the periods  $10^3$  and  $10^6$  years as estimated from the profiles shown in figure 2, we estimated the total amount released from a 3-ft-thick backfill, having a range of sorptive capacities, in a period of 1,000 years at the groundwater flow velocity of 1 ft/yr. As shown in table 2, a 3-ft-thick bed of backfill materials, such as zeolites having a sorption coefficient of 10<sup>4</sup> ml/g, will contain practically all the inventory released from the waste for a period of up to 1,000 years. This implies that a discrete zeolite backfill will satisfy the NRC 1,000 year containment criterion. Table 3 shows calculated results of fractional controlled release rate from a 10- and a 100-ft-thick backfill bed over a period  $10^6$  years. In these calculations, the assumptions made for the source term and backfill are the same as those described in table 2. Assuming a leach rate of less than  $10^{-3}$  g/cm<sup>2</sup>-yr and a surface area of the glass monolith to be 3.6 x  $10^4$  cm<sup>2</sup>, the NRC controlled release criteria can be met using a >10-ftthick non-discrete zeolite backfill bed for periods of up to 10<sup>b</sup> years. These calculations show the significance of a waste form having a low leach rate with respect to meeting the controlled release criterion. In such a situation, the sole purpose of the backfill would be to control water ingress in order to minimize the probability of container corrosion. It must be emphasized that bulk fluid flow, based on a groundwater velocity of 1 ft/yr, also contributes

to radionuclide transport. In a realistic repository situation, the flow velocities are much smaller than that assumed in our calculations. In that case, the transport would be predominantly diffusion-controlled, resulting in a more effective containment by the backfill barrier.

Using model 2 and making the same assumptions for the source term and backfill barrier, we obtained estimates of the total amount of activity released from a 3-ft-thick backfill barrier in a period of  $10^3$  years. As shown in table 4, the calculated values indicate that the 1,000 year containment criterion will be met by a 3-ft-thick bed of backfill with sorption coefficients in the range of  $10^4$  ml/g. Also included in table 4 are values for fractional amounts of activity released from the backfill barrier in 1,000 years.

Using the same model and considering a time period of  $10^5$  years and bed thicknesses of 3 ft and 10 ft, we obtained estimates of fractional release per year from the backfill bed (table 5). The results show that for backfill materials having sorption coefficients in the range of  $10^4$  ml/g, the annual fractional release from 3-ft-and 10-ft-thick beds are  $10^{-5}/yr$  and  $10^{-6}/yr$ , respectively. This indicates that the controlled release criterion of  $10^{-5}/yr$  will be met by highly sorptive backfill materials such as synthetic zeolites and/or titanates for long period of time.

Model Calculation for Total U.S. Waste Inventory

In order to demonstrate the effectiveness of backfill as a barrier to radionuclide migration, we assumed the source term to be the total U.S. waste inventory and calculated the total thickness of backfill that would be required to provide controlled release rate over a period of 10<sup>6</sup> years.

Using models 1 and 2, we used a value of  $10^9$  Ci [23] for the total waste inventory in the U.S. [12] and 100- and 200-ft for bed thicknesses. The calculated estimates of radionuclide release are compiled in tables 6 and 7. Table 6, based on model 1, shows that the annual release from 200-ft-thick backfill, having a sorption coefficient of  $10^4$  ml/g, is on the order of  $10^{-80}$  Ci/yr. This indicates that the total containment will be achieved during this period. Table 7, based on model 2, also shows that a 200-ft-thick bed of backfill  $(K_d = 10^4 \text{ ml/g})$  will provide total containment. A bed thickness of 100 ft, however, is not sufficient to obtain the desired containment.

### CONCLUSIONS

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For groundwater velocities below 1 ft/yr, diffusion and sorption are the dominant processes controlling radionuclide migration in highly sorptive backfill materials such as synthetic zeolites. A 3-ft-thick bed of synthetic zeolite backfill can provide total containment of activity released continuously from a 55-gallon glass monolith for a period of up to 1,000 years. For longer time periods of up to  $10^6$  years, the controlled release rate of  $10^{-5}/yr$  can be met by a >10-ft-thick bed of zeolite backfill, assuming the glass monolith to be the source term. In the absence of the waste form as an engineered barrier, a bed thickness of 3 to 10 ft is required to satisfy the controlled release criterion for a period of up to  $10^5$  years. With a bed thickness of 200 ft, synthetic zeolites can be used as backfill to provide containment of total U.S. waste inventory ( $10^9$  Ci), if it were placed in one repository, for periods of up to  $10^6$  years.

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Parameters Considered in Radionuclide Transport Calculations

Backfill Bed Thickness (ft): 1, 3, 10, 100 Transit Time (years): 1,000, 10,000, 100,000, 1,000,000 Sorption Coefficient (ml/g): 1, 10, 100, 1,00, 10,000 Ion Diffusion Coefficient (cm<sup>2</sup>/sec)[6]: 10<sup>-5</sup> Groundwater Velocity (ft/yr)[16,17,18]: 0, 1 Bed Porosity[19]: 0.34 Bed Density (g/cm<sup>3</sup>)[20]: 0.423

# Total Release of Radioactivity from a 3-ft-thick Backfill in 10<sup>3</sup> Years (Model 1)

Backfill Sorption Coefficient	Total Assumed Released from Backfill (Ci)		
Kd (m1/g)	$SA = 3.6 \times 10^4 (cm^2)$	$SA = 3.6 \times 10^{6} (cm^2)$	
100	$4 \times 10^4$	4 x 106a	
1,000	$4 \times 10^{0}$	$4 \times 10^2$	
10,000	5 x 10-46	$5 \times 10^{-44}$	

a Artificial number indicating total inventory release.

 $V_g = 1$  ft/yr; backfill thickness = 3 ft; leach rate (LR) =  $10^{-3}$  g/cm<sup>2</sup>-yr;  $C_o = LR \times SA \times transit time/area under the concentration curves;$ 

SA = surface area of the glass monolith.

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### Table 3

Fractional Release Rate from a 10-ft-and a 100-ft-Thick Backfill in 10<sup>6</sup> Years (Model 1)

		Fractional	Release Rat	e From Backf	ill (/yr)
Backfill	Sorption Coefficient	SA = 3.6	x 10 <sup>4</sup> (cm <sup>2</sup> )	SA = 3.6	$x  10^{6} (cm^{2})$
	Kd (ml/g)	10-ft	100-ft	10-ft	100-ft
	100	6.8 x 10 <sup>-5</sup>	6.7 x 10 <sup>-5</sup>	6.8 x 10 <sup>-3</sup>	6.7 x 10 <sup>-3</sup>
	1,000	6.7 x 10 <sup>-5</sup>	6.0 x 10 <sup>-5</sup>	6.7 x 10 <sup>-3</sup>	$6.0 \times 10^{-3}$
	10,000	6.0 x 10 <sup>-5</sup>	$3.6 \times 10^{-9}$	$6.0 \times 10^{-3}$	$3.6 \times 10^{-7}$

 $V_g = 1 \text{ ft/yr}; \text{ leach rate (LR)} = 10^{-3} \text{ g/cm}^2 - \text{yr};$ 

SA = surface area of the glass monolith.

# Fractional and Total Release from a 3-ft-Thick Backfill in 10<sup>3</sup> Years (Model 2)

Backfill Sorption Coefficient

5
2
-44

 $V_g = 1$  ft/yr, backfill thickness = 3 ft.

## Table 5

Fractional Release Rate from a 3-ft-Thick Backfill and a 10-ft-Thick Backfill in  $10^5$  Years (Model 2)

Backfill Sorption Coefficient	Fractional Release	se Per Year (/yr)
Kd (m1/g)	<u>3-ft</u>	10-ft
100	>10-5	>10-5
1,000	>10-5	>10-5
10,000	9.97 x 10-6	1.85 x 10-6

 $V_g = 1 \text{ ft/yr}$ .

# Annual Release From a 200-ft-Thick Backfill for 10<sup>6</sup> Years, Assuming the Source of Term to be Total U.S. HLW Inventory (Model 1)

Backfill Sorption Coefficient	Annual Release From	Backfill (Ci/yr)	
Kd (m1/g)	$SA = 2.4 \times 10^5 (cm^2)$	$SA = 2.4 \times 10^7$	(cm <sup>2</sup> )
100	4 x 102	4 x 104	
1,000	$3 \times 10^2$	3 x 104	
10,000	3 x 10 <sup>-80</sup>	3 x 10-78	

 $V_g = 1$  ft/yr; backfill thickness = 200 ft; leach rate (LR) =  $10^{-3}$  g/cm<sup>2</sup> yr; SA = surface area of all the glass monolith considered.

### Table 7

Annual Release From a 200-ft-Thick Backfill for 10<sup>6</sup> Years, Assuming the Source Term to be Total U.S. HLW Inventory (Model 2)

Backfill Sorption Coefficient	Annual Release From Backfill
Kd (ml/g)	(Ci/yr)
100	103
1,000	103
-	2
10,000	10-79
-	

 $V_g = 1 \text{ ft/yr}.$ 





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Figure 3. Concentration vs. bed thickness profiles for various transit times based on model 2: (a)  $K_d = 1000 \text{ ml/g}$ ,  $V_g = 0 \text{ ft/yr}$ ; (b)  $k_d = 100 \text{ ml/yr}$ ,  $V_g = 1 \text{ ft/yr}$ ;  $A = 10^3 \text{ yr}$ ,  $B = 10^4 \text{ yr}$ ,  $C = 10^5$ ,  $D = 10^6 \text{ yr}$ 

### APPENDIX 1

The simplified equation of the differential mass balance is

$$\frac{\delta c(x,t)}{\delta t} + \frac{V_g}{R_f} \frac{\delta c(x,t)}{\delta x} - \frac{D_f}{\sqrt{2} R_f} \frac{\delta^2 c(x,t)}{\delta x^2} = 0$$

where

$$R_{f} = \left(1 + \frac{\rho_{d} K_{d}}{\epsilon}\right)$$
, the retardation factor

x = the distance from the interface of the glass and the zeolite along the direction of flow and longitudinal diffusion (1)

t = time

- c(x,t) = liquid phase concentration, quantity of sorbing species per unit volume of liquid at distance along flow direction x and time t
  - ε = effective porosity of bed (fraction of bed volume containing flowing liquid)

 $V_g$  = average interstitial velocity of flowing water

- $D_f/\sqrt{2}$  = coefficient of longitudinal fluid diffusion with a tortuosity factor to account for the tortuous diffusion path through the porous bed
  - ρ<sub>b</sub> = the bulk packing density of solid sorbent, mass of solid per unit bed volume
  - Kd = the distribution coefficient for a linear sorption isotherm. The ratio of quantity of sorbed species per unit mass of solids to quantity of mobile species in the liquid phase per unit volume of liquid.

The boundary condition is

$$c(x = 0, t > 0) = C_{0}$$

The initial condition is

$$c(x > 0, t = 0) = 0.$$

Define

$$U(x,t) = c(x,t) \cdot \exp\left[\frac{-V_{g,x}}{\sqrt{2} D_{f}}\right] \cdot \exp\left[\frac{V_{g}^{2} \cdot t}{2\sqrt{2} \cdot D_{f} \cdot R_{f}}\right]$$

Then, Equation (1) is reduced to a heat equation of U(x,t) as function of x and t. With the rearrangement of boundary and initial conditions, the Fourier transform is applied to the heat equation, and the subsequent convolution gives the following solution

$$c(x,t)/C_{o} = 1 - \frac{1}{2} \left[ \operatorname{erfc} \left\{ \frac{V_{g} \cdot \sqrt{t}}{2^{3/4} \sqrt{D_{f} \cdot R_{f}}} - \frac{\sqrt{R_{f}} \cdot x}{2^{3/4} \sqrt{D_{f}} \cdot t} \right\} - \exp \left\{ \frac{\sqrt{2} V_{g} \cdot x}{D_{f}} \right\} \cdot \operatorname{erfc} \left\{ \frac{V_{g} \cdot \sqrt{t}}{2^{3/4} \sqrt{D_{f}} \cdot R_{f}} + \frac{\sqrt{R_{f}} \cdot x}{2^{3/4} \sqrt{D_{f}} \cdot t} \right\} \right]$$
(2)

where

erfc(y) = 1 - erf(y) and erf(y) is the error function of y.

The integration from x = backfill thickness to infinity is done numerically for the total release from backfill.

### **APPENDIX 2**

The same differential equation is used as in model 1. The new constraint instead of the boundary condition is

 $\int_{-\infty}^{\infty} C(x>0, t>0) dx = C_{total}$ 

and the new initial condition is

 $C(x > 0, t = 0) = C_{total} \delta(x)$ 

where  $\delta(x)$  is a delta function of x and  $C_{total}$  is a total quantity of sorbing species.

The transformation technique may not be plausible in this case for the closed form solution. However, since we know the response of step function from appendix 1, the response of the delta function should be the derivative of the response of the step function with respect to x: the derivative of equation (2) of appendix 1. Further, we need the integral from x equals the backfill thickness of infinity, which is equivalent to the response function of appendix 1 (equation 2).