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SORPTION-CAPACITY LIMITED RETARDATION OF RADIONUCLIDES TRANSPORT IN WATER-SATURATED PACKING MATERIALS

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ABSTRACT

Radionuclides breakthrough times as calculated through constant retardation factors obtained in dilute solutions are non-conservative. The constant retardation approach regards the solid as having infinite sorption capacity throughout the solid. However, as the solid becomes locally saturated, such as in the proximity of the waste form-packing materials interface, it will exhibit no retardation properties, and transport will take place as if the radionuclides were locally non-reactive. The magnitude of the effect of finite sorption capacity of the packing materials on radionuclide transport is discussed with reference to high-level waste package performance. An example based on literature sorption data indicates that the breakthrough time may be overpredicted by orders of magnitude using a constant retardation factor as compared to using the entire sorption isotherm to obtain a concentration-dependent retardation factor.

1. INTRODUCTION

As reactive constituents migrate in a water-saturated porous medium under the action of various transport mechanisms (diffusion, dispersion, advection), they undergo chemical reactions with the surface components of the solid matrix. If these reactions are reversible <u>and</u> take place at a much faster rate than the transport mechanisms under consideration, they can be modeled as equilibrium reactions between a liquid and a solid phase according to the overall reaction:

$$[I]\ (\text{liquid}) \overset{K_{eq}}{\rightleftarrows} [I]\ (\text{solid}) \qquad (1)$$

where "I" indicates a generic constituent of the flow stream. As a result of Reaction (1) some constituents become part, at least temporarily, of the solid phase and are not available for transport. Thus, as long as the solid is not fully saturated locally, the net effect is locally one of retardation of the transport process when compared to the nonreactive case.

Typically, if C indicates the concentration of species in solution and S indicates the mass of species on the solid phase per unit mass of the solid, this localized retardation effect is implemented in the diffusion-advection equation for non-reactive constituents in a homogeneous medium:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \lambda C \qquad (2)$$

by dividing each of the parameters D (diffusion-dispersion coefficient), u (linear velocity of the water), and λ (decay constant) by the retardation factor: [1]

$$R = R(C) = 1 + \frac{\rho_b}{n} \cdot \frac{dS}{dC} \qquad (3)$$

where:

ρ_b - bulk mass density of the porous medium;
n - porosity; and
$\frac{dS}{dC}$ - the ratio of the time rate of change of amount sorbed on the solid phase to the time rate of change of concentration of species in solution.

The higher the value of R, the higher is the local degree of retardation, as a larger R has the effect of locally decreasing the transport parameters D and u in Equation (2). The least amount of retardation occurs when dS/dC = 0.

Equation (3) is the reference expression for the retardation factor. It reproduces the classical expression:

$$R_{Cl} = 1 + \frac{\rho_b}{n} K_d \qquad (4)$$

when the amount sorbed, S, depends linearly on solution concentration, C, according to a relationship of the type:

$$S = K_d C, \qquad (5)$$

where K_d is the classical "distribution coefficient". However, typical radionuclide sorption isotherms are of the type displayed in Figure 1, i.e., they show a linear behavior at lower solution concentrations and a non-linear bendover at higher concentrations. This reflects a progressive loading of the porous solid, which also results in a monotonic decrease of the slope of the isotherm, dS/dC. Thus, while the classical approach would predict constant transport parameters over the entire range of solution concentrations, the general expression for retardation, Eqn (3), would predict somewhat higher transport parameters resulting in shorter solute breakthrough times.

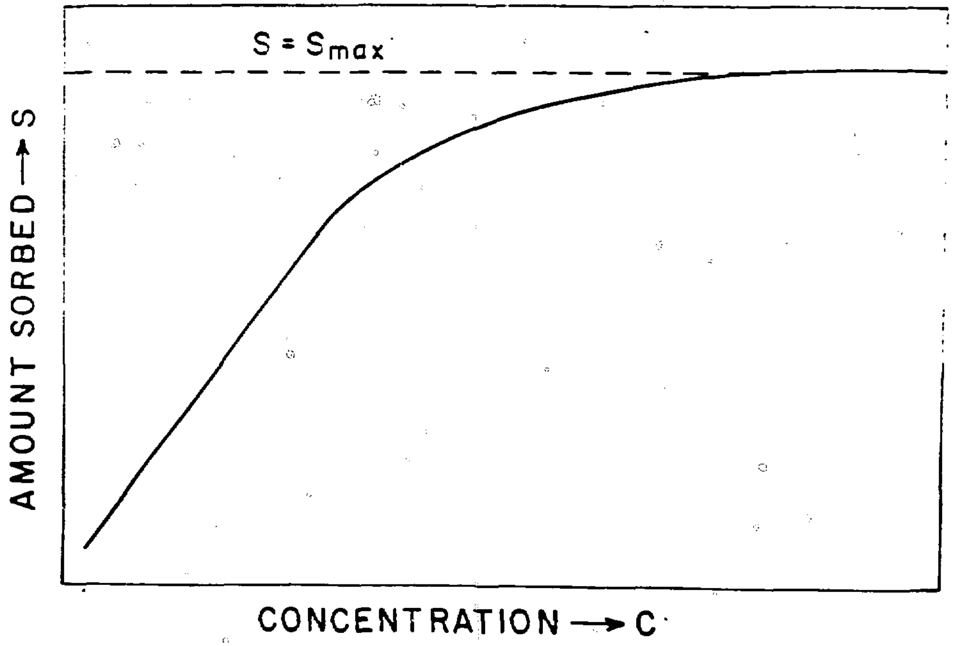

Figure 1. Typical partition of a solute between a porous solid and water (adapted from Ref. [1]).

The relevance of this effect to radionuclide transport is investigated in the remainder of this paper. Section 2 presents data available from the literature to illustrate the dependence of amount sorbed on solution concentration. Section 3 presents the results of a numerical, diffusive-type transport calculation which demonstrates the difference in breakthrough times based on the classical constant retardation factor and on the non-linear sorption isotherms as obtained from data presented in Section 2. Conclusions on the relevance of the difference in breakthrough times to waste package performance are discussed in Section 4.

2. SORPTION DATA

In order to explore the magnitude of the dependence of the retardation factor, Eqn (3), on solution concentration, we have examined recent literature data of radionuclide sorption on a clay soil [2] and in a basalt environment.[3,4,5]

The West Chestnut Ridge Data [2] are more comprehensive in that more data points for a wider range of concentrations are reported. Based on these data, a typical uranium sorption curve is shown in Figure 2. The actual data points along with calculated values of $\Delta S/\Delta C$ are reported in Table I. As it can be seen, this latter quantity varies over 3 orders of magnitude corresponding to an equivalent change in values of the retardation factor. Reference [2] reports similar curves for cesium, thorium, strontium, and europium.

The basalt sorption data [3,4,5] are more sparse, as only a few points are available for each sorption isotherm and the concentration range is limited. Thus, little information can be gained from those data on the non-linear portion of the isotherm. Reported curves for uranium and cesium, however, do display the typical bendover. This is shown for uranium in Figure 3. As reported in Table II, these data display a variation of two orders of magnitude in the quantity $\Delta S/\Delta C$, and, therefore, in the retardation factor.

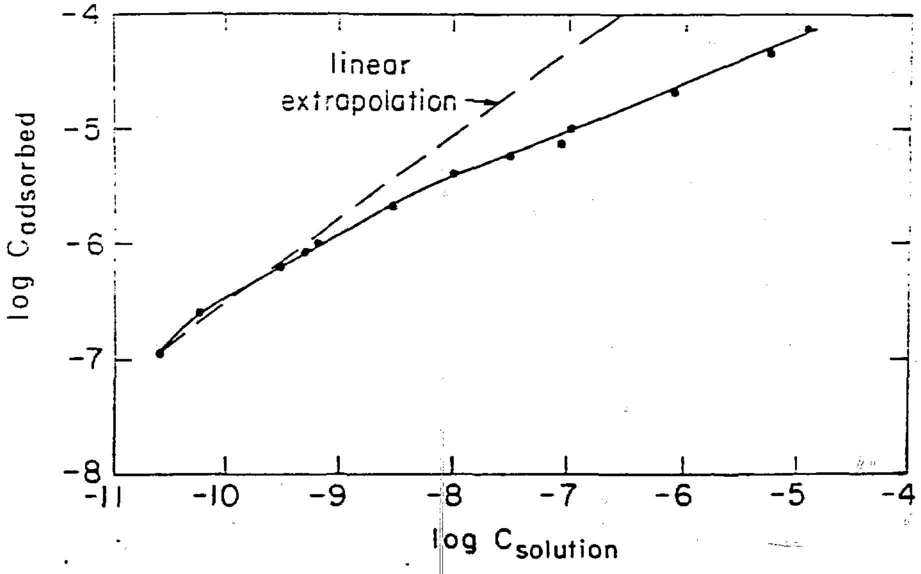

Figure 2. Uranium sorption data from West Chestnut Ridge (adapted from Table D-6 Ref. [2]).

Table I
Uranium sorption isotherm data for West Chestnut Ridge
(adapted from Table D-6 Ref. [2])

Solution, C (mol/L)	Adsorbed, S (mol/kg)	S/C (L/kg)	ΔS/ΔC (L/kg)
2.6×10^{-11}	1.1×10^{-7}	4.2×10^{3}	--
5.7×10^{-11}	2.3×10^{-7}	4.0×10^{3}	3.9×10^{3}
1.7×10^{-10}	4.5×10^{-7}	2.5×10^{3}	1.9×10^{3}
3.2×10^{-10}	6.4×10^{-7}	2.0×10^{3}	1.3×10^{3}
5.3×10^{-10}	8.6×10^{-7}	1.6×10^{3}	1.0×10^{3}
7.2×10^{-10}	1.0×10^{-6}	1.4×10^{3}	7.4×10^{2}
3.0×10^{-9}	2.1×10^{-6}	7.0×10^{2}	4.6×10^{2}
1.0×10^{-8}	4.1×10^{-6}	4.1×10^{2}	2.9×10^{2}
3.2×10^{-8}	6.0×10^{-6}	1.9×10^{2}	8.6×10^{1}
8.4×10^{-8}	8.0×10^{-6}	9.5×10^{1}	3.8×10^{1}
1.0×10^{-7}	9.9×10^{-6}	9.9×10^{1}	1.2×10^{1}
7.8×10^{-7}	1.7×10^{-5}	2.2×10^{1}	10.4
5.4×10^{-6}	4.1×10^{-5}	7.6	5.19
1.2×10^{-5}	7.5×10^{-5}	6.25	5.15

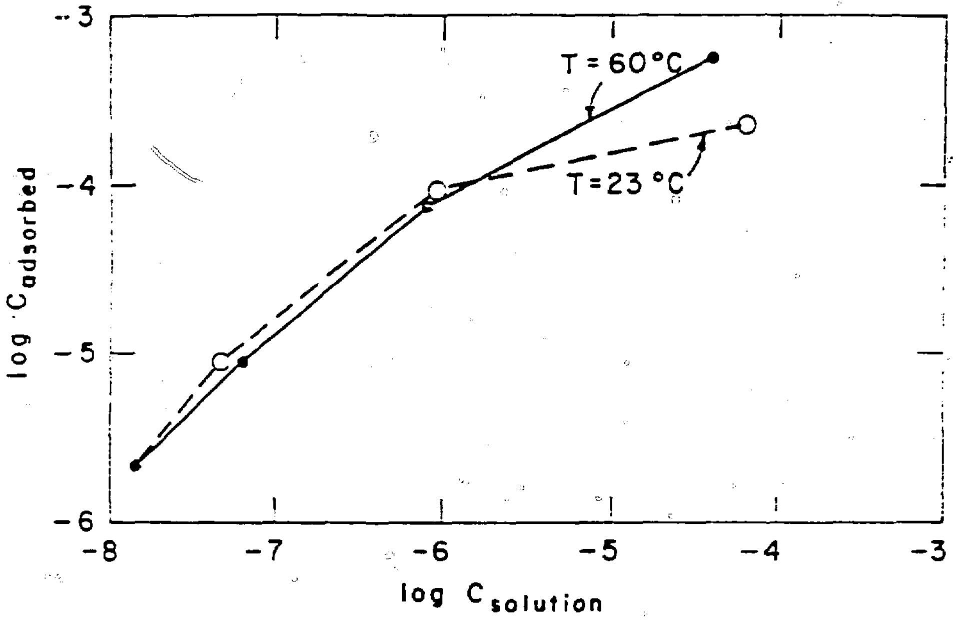

Figure 3. Uranium sorption data on Umtanum Basalt (adapted from Ref. [3]).

3. CALCULATION OF NUCLIDE TRANSPORT AS A FUNCTION OF THE RETARDATION COEFFICIENT

To examine the importance of using concentration-dependent retardation factors when determining the migration of radioactive species through water-saturated packing materials, numerical solutions of the diffusion equation have been performed using retardation factors obtained from the data of the previous section. For a repository, diffusion is expected to be the dominant mode of transport.[6]

Table II

Uranium sorption isotherm data for Umtanum basalt in a reducing environment (adapted from Ref. [3])

Solution, C (mol/L)	Adsorbed, S (mol/kg)	S/C (L/kg)	ΔS/ΔC (L/kg)	Comments
1.2×10^{-8}	2.3×10^{-6}	1.9×10^{2}	--	T=23°C
4.6×10^{-8}	9.5×10^{-6}	2.1×10^{2}	2.1×10^{2}	GR-1 synthetic
9.7×10^{-7}	9.0×10^{-5}	9.3×10^{1}	8.7×10^{1}	groundwater
7.7×10^{-5}	2.3×10^{-4}	3.0	1.8	
1.4×10^{-8}	2.3×10^{-6}	1.7×10^{2}	--	T=60°C
6.3×10^{-8}	9.4×10^{-6}	1.5×10^{2}	1.4×10^{2}	GR-1 synthetic
8.0×10^{-7}	9.2×10^{-5}	1.1×10^{2}	1.1×10^{2}	groundwater
4.0×10^{-5}	6.0×10^{-4}	1.5×10^{1}	1.3×10^{1}	

The numerical approach assumed a semi-infinite media, a solubility limited boundary condition at the waste-form packing materials interface and uncontaminated conditions far away from the waste form. Thus, neglecting advection and decay the transport equation, Eqn. (2), becomes:

$$\frac{\partial C}{\partial t} = \frac{D}{R(C)} \frac{\partial^2 C}{\partial x^2} \,, \qquad 0 < x < \infty,\ t > 0, \tag{6}$$

where R(C) is given by Eqn. (3).

The boundary conditions are:

$$C(0,t) = C_{sat}, \tag{7}$$

$$C(\infty,t) = 0 \,. \tag{8}$$

The initial condition is,

$$C(x,0) = 0. \tag{9}$$

Solution of Eqn. (6) was accomplished by first transforming the partial differential equation to a non-linear ordinary differential equation through the substitution

$$\zeta = x/\sqrt{2Dt} \,. \tag{10}$$

Using this substitution, Eqn. (6) becomes:

$$\frac{d^2C}{d\zeta^2} + \zeta\, R(C) \frac{dC}{d\zeta} = 0. \tag{11}$$

Solution of Eqn. (11) gives the concentration for all values of position, time, and diffusion coefficient as a function of the transformed variable, ζ. In the case where the retardation coefficient is constant, the analytic solution to Eqn. (11) is [7]:

$$C\,(\zeta) = C_{sat}\, \mathrm{erfc}(\zeta\, \sqrt{R}/2\,), \tag{12}$$

where erfc(x) is the complementary error function,

$$\mathrm{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2}\, dy \tag{13}$$

Four expressions for the concentration dependent retardation factors were examined in Eqn. (11) using the uranium sorption data presented in Table I. These expressions were generated through four different approximations to calculate the term dS/dC in Eqn. (3). Namely:

a) $\frac{dS}{dC} = \frac{\Delta S}{\Delta C}$

b) $\frac{dS}{dC} = \frac{S}{C}$ which represents the distribution coefficient, S/C, at the given solution concentration;

c) $\frac{dS}{dC} + 4.2\text{x}10^3$ which represents the distribution coefficient, S/C, at low solution concentrations; and

d) $\frac{dS}{dC} = 6.25$ which represents the distribution coefficient at the highest experimentally measured solution concentration and is the minimum value for S/C.

In solving Eqn. (11), it was assumed that the highest measured solution concentration corresponded to the saturation concentration, C_{sat}, at $\xi=0$. The porosity, n, was chosen as 0.2 representing loosely compressed packing material with a bulk density of $\rho_b=2$ g/cm^3. Using these values, Eqn. (11) was solved for cases a) – d).

The influence of the various approximations for the term dS/dC is illustrated through the breakthrough times, defined as the time at which the concentration at a given position is a fixed fraction of C_{sat}, the concentration at the boundary x=0. For comparative purposes, three breakthrough concentrations, 0.5 C_{sat}, 0.1 C_{sat}, and 0.05 C_{sat}, were selected.

The results of the various calculations are reported in Table III where breakthrough times are normalized to the breakthrough time calculated for the most correct approximation, dS/dC=ΔS/ΔC. If the ratio presented in Table III is greater than 1 the breakthrough time is non-conservative in comparison. From Table III, it is clear that the use of dilute solution distribution coefficient, approximation (c), leads to predicted breakthrough times over 500 times longer than the reference value. Use of S/C, approximation (b), to obtain the retardation factor overpredicts the breakthrough time by less than a factor of 2. Using a constant value of dS/dC based on the distribution coefficient at the highest solution concentration, case (d), is more conservative than the reference case, as expected, and as illustrated by the lower breakthrough concentrations. At the highest breakthrough concentration, C=0.5 C_{sat}, the reference case is more conservative because ΔS/ΔC is initially less than $(S/C)_{min}$. In fact, in the concentration range of 0.5 C_{sat} to C_{sat}, ΔS/ΔC ranges from 5.15 to 5.20 which is less than $(S/C)_{min}$ which is 6.25. Thus, in this range of concentrations, the ΔS/ΔC approximation yields less retardation and therefore shorter breakthrough times. This illustrates that using $(S/C)_{min}$ does not always predict the quickest breakthrough time. However, in this example as the solution concentration decreases ΔS/ΔC increases to values greater than $(S/C)_{min}$, and case (d) becomes the more conservative approximation.

As an example of the magnitude of the predicted differences in breakthrough times consider a diffusion coefficient of 10^{-10} m^2/s, a backfill thickness of 0.15 m, and a breakthrough concentration of 0.05 C_{sat}. In this case and for dS/dC=ΔS/ΔC the calculated value for the transformed variable was $\xi=0.2273$. Using these values, the calculated breakthrough times are:

a) $\frac{dS}{dC} = \frac{\Delta S}{\Delta C}$, t = 69 years;

b) $\frac{dS}{dC} = \frac{S}{C}$, t = 109 years;

c) $\frac{dS}{dC} = 4230$, t = 39,280 years; and,

d) $\frac{dS}{dC} = 6.25$, t = 58 years.

The preceding example is particularly dramatic because of the large change in dS/dC and therefore, in the retardation factor over the range of solution concentrations. However, similar effects still occur for smaller changes, since an order of magnitude decrease in the retardation factor produces roughly an order of magnitude decrease in breakthrough time.

Although not explicitly shown here, similar results can be expected when advection becomes an important transport process.

In general, if the retardation coefficient approach is used in calculating migration of species, both in the packing material and the host rock, care must be exercised to insure that conservatism is guaranteed. This applies to both the proper use of the data, the subject of this paper, and use of the proper data. With regards to the latter, sorption phenomena are extremely sensitive to groundwater chemistry, properties of the sorbing material, and environmental conditions such as temperature, Eh, and pH.[4] Thus, large differences in measured distribution coefficients can be found in the literature. Furthermore, the data assume equilibrium between the sorbing media and the groundwater. This may not be true in experiments conducted over a few weeks.[8]

Table III
Breakthrough times normalized to breakthrough time based on $R=1+(\rho_b/n)\ \Delta S/\Delta C$.

		Breakthrough Concentration	
dS/dC	0.5 C_{sat}	0.1 C_{sat}	0.05 C_{sat}
$\Delta S/\Delta C$	1.0	1.00	1.00
S/C	1.3	1.57	1.58
4.2×10^3	802.0	646.00	569.00
6.25	1.2	0.97	0.85

4. CONCLUSION

Retardation of nuclide transport is a local concept which depends on the local chemistry. In regions where the solution concentration is high, sorption isotherms that show bendover are common, particularly for the actinides. This suggests retardation may be a few orders of magnitude less than in dilute solutions. As shown in the previous section, use of the full isotherm to obtain the retardation coefficient used in the diffusion equation leads to a prediction of shorter solute breakthrough times than the classical constant retardation coefficient based on retardation in dilute solutions. This is of importance in near field waste package performance when calculating release of radionuclides.

If credit is given for retardation, the retardation factors must be conservative. This will require that the entire sorption isotherm is explored and used in the calculations, and that the experimental conditions used while generating the data are pertinent to expected repository conditions. This implies the complex chemistry expected upon leaching of a waste form should be simulated as closely as possible when obtaining sorption data. In any event, unless it can be shown that the solution will be dilute with respect to a given species, constant retardation factors based on experimental results in dilute solutions should not be used to determine the retardation factor.

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