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# Multi-regime transport model for leaching behavior of heterogeneous porous materials

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## Abstract

Utilization of secondary materials in civil engineering applications (e.g. as substitutes for natural aggregates or binder constituents) requires assessment of the physical and environment properties of the product. Environmental assessment often necessitates evaluation of the potential for constituent release through leaching. Currently most leaching models used to estimate long-term field performance assume that the species of concern is uniformly dispersed in a homogeneous porous material. However, waste materials are often comprised of distinct components such as coarse or fine aggregates in a cement concrete or waste encapsulated in a stabilized matrix. The specific objectives of the research presented here were to (1) develop a one-dimensional, multi-regime transport model (i.e. MRT model) to describe the release of species from heterogeneous porous materials and, (2) evaluate simple limit cases using the model for species when release is not dependent on pH. Two different idealized model systems were considered: (1) a porous material contaminated with the species of interest and containing inert aggregates and, (2) a porous material containing the contaminant of interest only in the aggregates. The effect of three factors on constituent release were examined: (1) volume fraction of material occupied by the aggregates compared to a homogeneous porous material, (2) aggregate size and, (3) differences in mass transfer rates between the binder and the aggregates. Simulation results confirmed that assuming homogeneous materials to evaluate the release of contaminants from porous waste materials may result in erroneous long-term field performance assessment. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Increased interest in utilization of waste materials in civil engineering works (e.g. coal fly ash in concrete, incineration slag in road construction) and concern over the long-term environmental performance of systems utilizing such secondary materials has resulted in the need for more accurate assessments of constituent leaching. This includes understanding the leaching behavior of primary matrix components that may be indicative of both structural and environmental performance. Similarly, selection of appropriate solidification/stabilization treatment processes for waste disposal, without requiring excessive treatment because of unknown safety margins, requires assessment of long-term contaminant release.

Currently, most models, based on diffusion controlled release or coupled dissolution and diffusion, use laboratory leaching data to estimate long-term field performance assuming the constituents of concern in cement stabilized systems are uniformly dispersed in a homogeneous matrix (Barna et al., 1997; Batchelor, 1992; Baverman et al., 1997; Hinsenveld, 1992; Kosson et al., 1996; Moszkowicz et al., 1998; Sanchez et al., 2000). However, the actual physical system is often comprised of distinct components such as coarse or fine aggregates in cement concrete or waste encapsulated in a stabilized matrix (e.g. slag incorporated in a cement-based matrix). Constituents of concern may be present in either or both of the physical components (i.e. binder or aggregate). Rates of chemical and mass transfer processes can vary by orders of magnitude between the components. Misrepresentation of the physical system may result in erroneous long-term performance assessments. Thus, it is therefore necessary to consider a

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multi-regime transport model for accurate long-term leaching assessments.

The specific objectives of the research presented here were to (1) develop a one-dimensional, multi-regime transport model (i.e. MRT model) to account for the different components of heterogeneous porous materials, and (2) evaluate simple limit cases using the model for species when release is not dependent on pH, to illustrate the impact of heterogeneous porous materials on contaminant release.

## 2. Multi-regime transport model development

### 2.1. Mathematical modeling

The heterogeneous porous materials were assumed to consist of two distinct physical components (i.e. aggregates and binder). Constituents of interest may be present in either or both components. Model development was adapted from an approach previously used for an analogous system (Arands et al., 1997) to describe VOC fate in soils and based on the conceptual diagram shown in Fig. 1. The porous solid matrix was modeled as two distinct homogeneous compartments: (1) a compartment made of binder in which mass transport of the species of interest towards the leaching solution occurs by diffusion and (2) a compartment made of a uniform distribution of aggregates which acted as sources or sinks for the species of interest. A one-dimensional geometry of thickness 2d was considered for the binder compartment. The aggregates were modeled as spheres within which transport occurred by diffusion. The MRT model assumes that there is no interface reaction

between the aggregates and the binder. In this stage of development, the MRT model is only valid to describe the release from a heterogeneous porous material of species when leaching behavior is not a function of pH (e.g. Na, Cl) or when no pH gradient within the material is generated during the leaching. For these cases, species release is controlled only by diffusion. When mass transfer of the species of interest is pH dependent more sophisticated models than the simple Fickian diffusion model used here are necessary to account for phenomena such as dissolution/precipitation (Baker and Bishop, 1997; Batchelor, 1990, 1992, 1998; Batchelor et al., 1993; Cheng and Bishop, 1990; Hinsenveld, 1992; Hinsenveld et al., 1996; Moszkowicz et al., 1996, 1997; Sanchez, 1996).

Using the conservation principle and Fick's law, mass transport of the species of interest within the binder in one-dimension is given by:

$$\frac{\partial C_{\text{Binder}}}{\partial t} = D_{e, \text{Binder}} \times \frac{\partial^2 C_{\text{Binder}}}{\partial x^2} + \frac{1}{\left(1 - \sum_{j=1}^m f_{\text{Agg},j}\right)} \times \sum_{j=1}^m (f_{\text{Agg},j} \times q_{\text{Agg},j}) \quad (1)$$

where,

- $C_{\text{Binder}}$  Species concentration in the binder (mass/m<sup>3</sup> binder);
- $D_{e, \text{Binder}}$  Effective diffusivity of the species of interest in the binder (m<sup>2</sup>/s);
- $q_{\text{Agg},j}$  Flux from aggregate type  $j$  (mass/m<sup>3</sup> aggregate s);

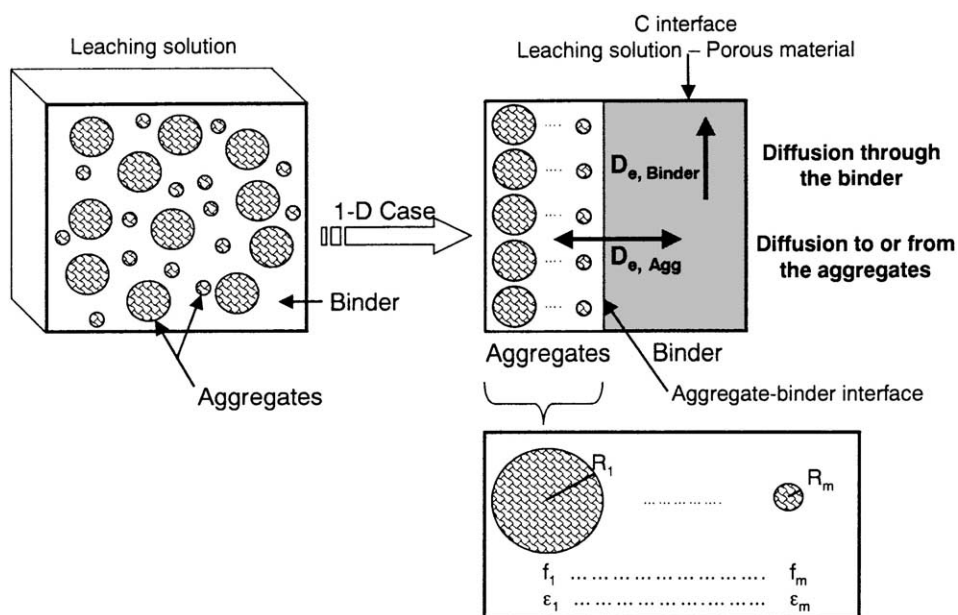


Fig. 1. Conceptual model for a non-homogeneous porous material.

$f_{\text{Agg},j}$	Volume fraction of aggregate type $j$ ( $\text{m}^3$ aggregate/ $\text{m}^3$ porous material);
$m$	Total number of aggregate types;
$t$	Time (s); and,
$x$	Linear coordinate (m).

Mass transport of the species of interest within an aggregate of radius  $R$  is given by:

$$\frac{\partial C_{\text{Agg},j}}{\partial t} = D_{e,\text{Agg},j} \times \frac{1}{r^2} \times \left[ \frac{\partial}{\partial r} \left( r^2 \times \frac{\partial C_{\text{Agg},j}}{\partial r} \right) \right] \quad (2)$$

where,

$C_{\text{Agg},j}$	Species concentration in aggregate type $j$ (mass/ $\text{m}^3$ aggregate);
$D_{e,\text{Agg},j}$	Effective diffusivity of the species of interest in aggregate type $j$ ( $\text{m}^2/\text{s}$ );
$t$	Time (s); and,
$r$	Radial coordinate (m).

### 2.2. Initial and boundary conditions

The species of concern is assumed to be initially present at uniform concentration  $C_{0,\text{Binder}}$  within the binder and uniform concentration  $C_{0,\text{Agg},j}$  within the aggregates.

$$C(x)_{\text{Binder}} = C_{0,\text{Binder}} \quad \text{for all } x, t = 0 \quad (3)$$

$$C(r)_{\text{Agg},j} = C_{0,\text{Agg},j} \quad \text{for all } r, t = 0 \quad (4)$$

The boundary condition at the binder compartment interface with the leaching solution (finite bath) is provided by mass balance within the leaching solution and is given by:

$$V \times \frac{\partial C_{\text{Leachate}}}{\partial t} = A \times D_{e,\text{Binder}} \times \frac{\partial C(x)_{\text{Binder}}}{\partial x} \Big|_{x=0} \quad (5)$$

$V$	Volume of the leaching solution (L);
$A$	Surface area of the matrix in contact with the leaching solution ( $\text{m}^2$ ); and,
$C_{\text{Leachate}}$	Concentration in the leaching solution (mass/L of leaching solution).

The boundary condition at the centerline of the binder compartment (i.e.  $x=d$ ) is expressed as a “no flux” condition [Eq. (6)].

$$\frac{\partial C(x)_{\text{Binder}}}{\partial x} \Big|_{x=d} = 0 \quad \text{for all } t, x = d \quad (6)$$

The concentration at the aggregate interface with the binder ( $C(R)_{\text{Agg},j}$ ) is given by the concentration profile within the binder.

$$C(R)_{\text{Agg},j} = C(x)_{\text{Binder}} \quad \text{for all } t \text{ and } x, r = R \quad (7)$$

### 2.3. Model sequence and numerical method

The MRT model is accomplished by dividing the computation into two stages: (1) calculation of the flux to or from the aggregates based on diffusion through spheres of radius  $R$  [Eq. (2)] and, (2) calculation of species transport by diffusion through the binder [Eq. (1)] using the local aggregate flux calculated by the aggregate equation. The resulting concentration profile within the binder then is used to form the boundary conditions for the aggregate equation. These two steps are repeated until the convergence of the solution is obtained. The overall release flux of the species of concern is then calculated for the boundary between the bulk material and the external leaching solution.

The height (2d) of the 1-D binder compartment is discretized into  $n_{\text{Binder}}$  slices. Within each binder slice, a distribution of aggregates is assumed. Each aggregate is discretized into  $n_{\text{Agg}}$  slices (concentric spherical shells). The mass transport equations within the binder and within each aggregate (i.e. partial differential equations) were converted to arithmetic equations using a fully implicit central difference scheme in space and Euler’s time marching method.

### 3. Model systems and theoretical study

Two different model systems were evaluated using the model:

Model system 1. Porous material (binder) contaminated with the species of interest and containing inert aggregates (i.e. the species of interest is initially only found in the binder and there is no diffusion of the species through the aggregates); and,

Model system 2. Porous material (binder) containing the contaminant of interest only in the aggregates.

These model systems were used to examine the effect of three factors on the contaminant release: (1) volume fraction of material occupied by the aggregates compared to a homogeneous porous material, (2) aggregate size and, (3) differences in mass transfer rates between the binder and the aggregates. For these purposes, three different volume fractions of aggregates (i.e. 0, 30 and 70%) and four different aggregate sizes (i.e. spheres of 0.15, 2.5, 5 and 10 mm radius) were used. Three different diffusivity ratios ( $D_{e,\text{Binder}}/D_{e,\text{Agg}}$ ) were used to simulate the cases where the diffusion in the aggregates was (1) much slower than in the binder, (2) much faster than in the binder and, (3) the same as in the binder. Observed diffusivity values used in the simulations are shown in Table 1. Simulations were carried out considering blocks of  $10 \times 10 \times 10$  cm in contact with water on only

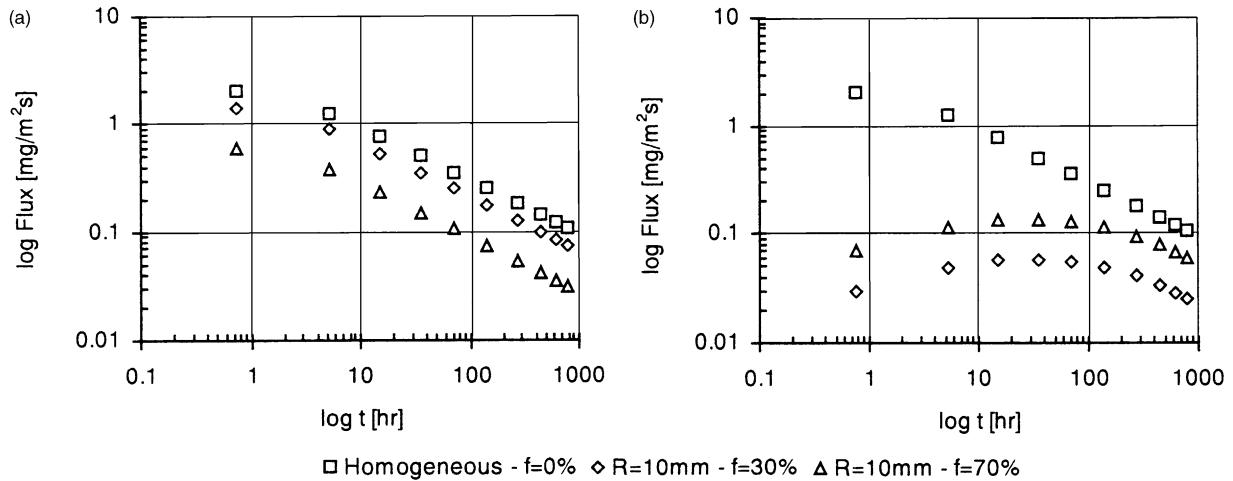


Fig. 2. Released flux as a function of volume fraction of material occupied by the aggregates. (a) Model system 1 ( $D_{e,Binder} = 10^{-11} \text{ m}^2/\text{s}$ ;  $D_{e,Agg} \ll D_{e,Binder}$ ) and, (b) model system 2 ( $D_{e,Binder} = D_{e,Agg} = 10^{-11} \text{ m}^2/\text{s}$ ).

one face using a liquid to surface area ratio of 10 cm, and periodic renewals of the leaching solution at intervals of 3, 5, 16, 24, 48, 96, 168 and 168 h (i.e. typical leaching intervals used in laboratory testing) resulting in a cumulative leaching time of 5 weeks.

4. Results and discussions

4.1. Effect of the volume fraction of material occupied by the aggregates

Simulations results obtained using three different volume fractions of aggregates (i.e. 0, 30 and 70%) and considering the aggregates as spheres of 10-mm radius are shown in Figs. 2a and b for model system 1 and model system 2, respectively. For model system 1, the diffusivity ratio ( $D_{e,Binder}/D_{e,Agg}$ ) was taken large enough to comply with the assumption of inert aggregates (i.e. no diffusion of the species through the aggregates). For model system 2, the diffusivity ratio was set to one. Zero percent represented the case of a homogeneous porous material uniformly contaminated with the species of interest. The simulations for model system 1 exhibited

expected patterns that were similar for all cases, including the homogeneous case (i.e. straight line with a slope of  $-0.5$ ) with the intensity of the flux decreasing as the volume fraction of aggregates increased. The simulations for model system 2 exhibited an initial delay in the release flux as a result of mass transport through the binder and the overall flux intensity increased as the volume fraction of aggregates increased.

4.2. Effect of aggregate size

Simulations results obtained for model system 1 and model system 2 using four different aggregate sizes (i.e. spheres of 0.15, 2.5, 5 and 10 mm radius) and considering a volume fraction of aggregates of 30% are shown in Fig. 3 for both model systems. The diffusivity ratio ( $D_{e,Binder}/D_{e,Agg}$ ) was taken large enough for model system 1 (i.e.

Table 1  
Effective diffusivity values used for the simulations carried out using model system 1 and model system 2

	$D_{e,Binder}$ ( $\text{m}^2/\text{s}$ )	$D_{e,Agg}$ ( $\text{m}^2/\text{s}$ )
Model system 1 <sup>a</sup>	$10^{-11}$	–
Model system 2		
$D_{e,Binder}/D_{e,Agg} = 1$	$10^{-11}$	$10^{-11}$
$D_{e,Binder}/D_{e,Agg} = 10^{-5}$	$10^{-16}$	$10^{-11}$
$D_{e,Binder}/D_{e,Agg} = 10^{+5}$	$10^{-11}$	$10^{-16}$

<sup>a</sup> The aggregates were assumed to be inert. No diffusion through the aggregates was considered for system 1.

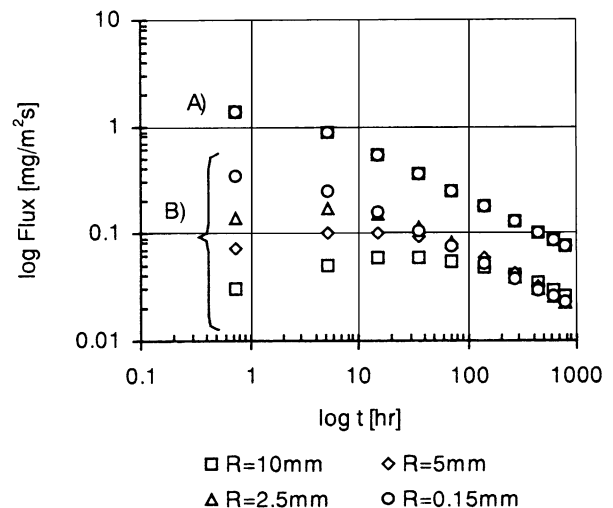


Fig. 3. Released flux as a function of aggregate size. (A) Model system 1 ( $D_{e,Binder} = 10^{-11} \text{ m}^2/\text{s}$ ;  $D_{e,Agg} \ll D_{e,Binder}$ ) and, (B) Model system 2 ( $D_{e,Binder} = 10^{-11} \text{ m}^2/\text{s}$ ).

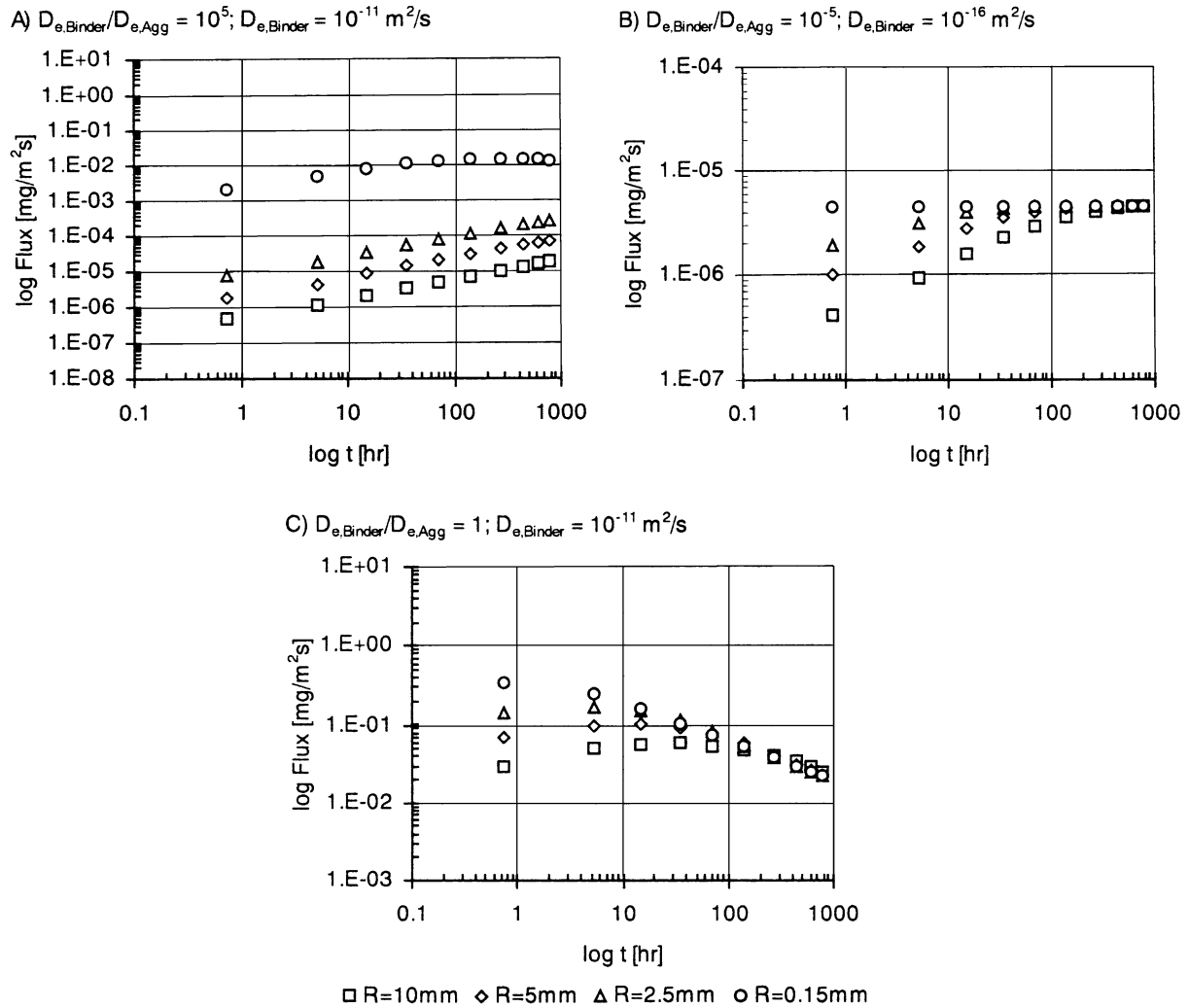


Fig. 4. Released flux when diffusion in the aggregates was (A) much slower than in the binder; (B) much faster than in the binder and, (C) the same as in the binder.

$D_{e,Agg} \ll D_{e,Binder}$ ) and set to one for model system 2. For model system 1, no effect of aggregate size was observed. Model system 2 showed lower release flux as aggregate size increased until mass transfer through the binder was no longer the limiting factor.

#### 4.3. Effect of differences in mass transfer rate between the components

Simulations were carried out on the model system 2 considering a volume fraction of aggregates of 30% and four different aggregate sizes (i.e. spheres of 0.15, 2.5, 5 and 10 mm radius). Three diffusivity ratios [i.e. ( $D_{e,Binder}/D_{e,Agg}$ ) equal to  $10^5$ ;  $10^{-5}$  and 1] were used to simulate, respectively, the cases where the diffusion within the aggregates was (1) much slower than, (2) much faster than and, (3) the same as in the binder. When diffusion in the aggregates was much slower than in the binder (i.e. mass transfer limitation within the aggregates), a significant increase in the released flux was observed

followed by a constant flux (Fig. 4A). The same behavior of the flux was observed when diffusion in the aggregates was much faster than in the binder (i.e. mass transfer limitation within the binder) but shifted in time and intensities (Fig. 4B). When diffusion in the aggregates was the same as in the binder (Fig. 4C), the released flux showed an initial delay due to the initial mass transport through the binder followed by a similar pattern as the flux obtained for the homogeneous material (i.e. straight line with a slope of  $-0.5$ ). Similar results will be obtained in the case of much lower diffusivity values than the ones used here, with lower flux intensity and longer time required to reach a proper stable release. This result is quite important for the time scale of laboratory testing. In the case of large differences between binder and aggregate diffusivity, testing time to reach a proper stable release after an initial delay may not be reasonably achievable in the laboratory and the modeling approach presented here becomes an important tool for long-term release assessment.

## 5. Conclusions

The impact of heterogeneous porous materials on contaminant release has been examined for simple limit cases when release is not dependent on pH. The MRT model presented in this paper is valid when species release is controlled only by diffusion. When the mass transport behavior of the species of interest is dependent on pore solution pH, then more sophisticated models are required to account for phenomena such as dissolution/precipitation.

The theoretical results obtained using the MRT model showed that in the case of a porous material contaminated with the species of interest and containing inert aggregates (i.e. the species of interest is initially only found in the binder and there is no diffusion of the species through the aggregates), the released flux is a fraction of the flux obtained in the homogeneous case and is proportional to the volume fraction of material occupied by the binder as would be expected. However, in the case of a porous material containing contaminated aggregates (i.e. the species of interest is initially only found in the aggregates), an initial delay in release as well as increases in the released flux or constant flux could be observed, indicating that prediction of species release based on the assumption of an homogeneous porous material may result in significant errors. In that case, long-term release prediction cannot be accomplished by using a simple correction factor to compensate for matrix heterogeneity, but it is necessary to use a multi-regime transport model.

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