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# Mathematical model development and simulation of in situ stabilization in lead-contaminated soils

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## Abstract

Stabilization and remediation of lead-contaminated soils has received considerable attention recently. Amending Pb-contaminated soils with phosphate as an in situ remediation option has been proposed as an alternative to other remediation options, such as soil removal. Research shows that hydroxyapatite (HA)  $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$  can reduce the bioavailability of Pb efficiently and thus is considered as an ideal phosphate source for formation of lead pyromorphite. Environmental models are increasingly being relied upon to help identify the limiting factors in such kind of in situ remediation.

In this work, the contaminated aggregates remediation model has been developed and simulated to describe the effects of initial contaminant concentration, diffusion coefficient, and aggregate diameter on the time of remediation which is defined as the time required to reduce the aqueous phase lead concentration to  $<1$  ppb. Results of simulation demonstrate that the aggregate size plays a significant role in remediation. The compartments-in-series model has been used to describe the dynamics of in situ stabilization in a soil bed. Results show that for a shallow bed a single, well-mixed, one compartment model gives approximately the same remediation time as the three compartments-in-series model. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Modeling; Stabilization; Remediation; Hydroxyapatite; Lead pyromorphite

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## 1. Introduction

Lead (Pb) is a heavy metal and is potentially toxic to humans. Numerous cases of Pb-contaminated soil and waste have been reported due to its extensive use and widespread distribution in the environment. Among these, soil removal is often the preferred method for Pb-contaminated materials in residential areas. Options for excavated materials include

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### Nomenclature

$a$	interfacial area of the aggregate per unit volume of the bed (l/m)
$c_A$	concentration of HA in the liquid phase (kg/m <sup>3</sup> or g mol/m <sup>3</sup> )
$c_A^0$	concentration of HA in the entering bulk liquid (kg/m <sup>3</sup> )
$c_B$	the concentration of lead compound in solid phase (mg/kg)
$c_B^0$	initial concentration of lead compound in solid phase (mg/kg)
$c_P$	the concentration of pyromorphite in the solid phase (mg/kg)
$D$	diameter of the particle (m)
$D_A$	effective diffusion coefficient (m <sup>2</sup> /s)
$D_i$	initial diameter of the particle (m)
$J$	rate of mass transfer from the mobile liquid to the aggregates (kg/m <sup>2</sup> s)
$k_r$	reaction rate constant (l/s)
$M_B$	molecular weight of lead compound (g/mol)
$M_P$	molecular weight of lead pyromorphite (g/mol)
$Q$	volumetric flow rate in the bed (m <sup>3</sup> /s)
$r$	radial position (m)
$R$	radius of the aggregate (m)
$r_A$	rate of reaction of hydroxyapatite A (g mol/m <sup>3</sup> s)
$r_B$	rate of reaction of lead compound B (g mol/m <sup>3</sup> s)
$r_P$	rate of reaction of pyromorphite (g mol/m <sup>3</sup> s)
$t$	time (min)
$t_R$	mean fluid residence time in the bed (min)
$V$	volume of the bed (m <sup>3</sup> )

### Greek letters

$\varepsilon_a$	volumetric fraction of liquid in the aggregate
$\varepsilon_1$	volumetric fraction of macropore void volume in the soil bed
$\rho$	density of the aggregate (kg/m <sup>3</sup> )
$\tau$	tortuosity factor to account for retardation of diffusion in the pores in the aggregate

### Superscripts and subscripts

ml	mobile liquid
pl	pore liquid
$j$	compartment number

solidification, vitrification, washing, leaching and particle size separation [1]. The methods have a significant drawback given that the volume of material that requires treatment or removal can be quite large. Furthermore, those methods are costly, disruptive and not sustainable.

Recently, the idea of amending Pb-contaminated soils with phosphorus as an in situ remediation option has been proposed. It has been recognized for some time that lead phosphates and in particular pyromorphite (P), are one of the most stable forms of Pb in the

environment [2]. Lead reacts with soluble P to form various pyromorphite minerals that are very insoluble in water. Research shows that pyromorphite is a natural weathering product in Pb-contaminated soils [3]. Suggestions of using P for immobilization of Pb in aqueous solutions and in soils soon followed [4–6]. The transport and reaction processes affecting the fate of lead contaminants during the stabilization of Pb with P amendments are fairly complex and intertwined. The knowledge of the rates of these processes is meager due to insufficient laboratory and field data. Therefore, it is highly desirable to evolve simplistic approaches, e.g. models, that can account for the mechanisms and represent the treatment scheme.

The majority of available transport models take into account the convection-dispersion flux by resorting to the classical convection-dispersion equations [7]. The analytical solutions for convective-dispersive transport in packed beds have been presented [8–10]. These and many other models consider the system to be homogeneous and isotropic [11,12]. The bimodal flow of contaminants has been explained by partitioning the porous media into two compartments, namely, mobile and immobile [13,14]. Little attention has been focused on the effect of aggregate characteristics in the bed.

The void in a porous medium typically is composed of a mobile phase in the relatively large pores, i.e. the macrovoids, and an immobile phase entrapped in the relatively small pores, which are called microvoids. Dispersion and convection dominate the transport in the macrovoids, whereas the transport in the immobile phase is driven by diffusion. The transport of solute through the aggregated medium has been simulated by Rao et al. [15,16] and Roberts et al. [17]. Pellet [18] and Satterfield et al. [19] have investigated the importance of diffusivity of solute and its adsorption in the aggregates for describing the dynamics of fixed beds. Thus pore diffusion needs to be considered in modeling the remediation of contaminants in soil aggregates.

The exact mechanisms responsible for the stabilization of Pb by  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (hydroxyapatite (HA)) are not clear, but available knowledge is necessary to understand the behavior of Pb in phosphate rich environments. The mechanism of reaction of Pb in soil with apatite has been studied recently [19–22]. Ma et al. proposed that dissolved Pb was removed from solution mainly through HA dissolution and  $\text{Pb}_5(\text{PO}_4)_3\text{OH}$  (pyromorphite) precipitation. Ma et al. further suggested that such a dissolution-precipitation process was the primary mechanism in the immobilization of Pb in the presence of apatite minerals and resulted in the formation of a carbonate fluoropyromorphite-type phase [23]. Three types of reactions may control Pb immobilization by HA: surface adsorption, cation substitution or precipitation. Experimental results show that hydroxypyromorphite was formed in the presence of HA at all pH values tested (pH = 3–7), which strongly supports the hypothesis of HA dissolution and hydroxypyromorphite formation. They also found that the removal of Pb from solution was not related to original surface area of calcium phosphate solids but rather to the total concentration of dissolved P. Thus, the effectiveness of HA or other P-containing minerals in reducing aqueous Pb was proportional to their solubilities. Results show that the immobilization process was rapid. Aqueous P concentration is the key factor in determining the effectiveness of Pb immobilization by apatite. As a result, pH also plays a role since it affects the solubility of apatite and Pb, Table 1.

Research shows that the pH and particle size are two important factors that affect the effectiveness of the remediation process. Ganguly et al. [24] developed a model to simulate

Table 1  
Properties of phosphate compounds<sup>a</sup>

pH	Solubility of hydroxyapatite Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH (mol/l)	Solubility of chloropyromorphite Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl (mol/l)
5	$6.30 \times 10^{-2}$	$1.58 \times 10^{-8}$
6	$3.16 \times 10^{-4}$	$3.98 \times 10^{-10}$
7	$1.58 \times 10^{-6}$	$1.99 \times 10^{-10}$
8	$5.01 \times 10^{-8}$	$1.58 \times 10^{-11}$

<sup>a</sup> Shi [28], Lindsay [29].

the leaching of metal from environmental soils by coupling reversible and irreversible chemical kinetics with a radial intraparticle diffusion model. Simulation results evidently show that the rate and extent of lead leaching are pH-dependent and at lower pH, there is a faster release of Pb. The simulation was conducted under three pH values (pH = 1–3). The Pb desorption occurs only at pH 1 near the particle surface, and the desorption front moves slowly into the particle pores at pH 1. At pH 3, Pb diffusion into the bulk solution is slow and retarded by adsorption of Pb ions. For the conditions and time frames considered in these simulations, diffusion, desorption, and the irreversible reaction processes each play an important role on lead removal in the pH range of 1–3. Particle size determines whether the diffusion effects are important or not. According to their research, the extent to which diffusion affects the remediation process is related inversely to the value of  $D_m/R^2$ , where  $D_m$  is the metal pore diffusion coefficient and  $R$  the particle radius. For larger particles, diffusion effects are more important.

Although, some models dealing with the fate and transport of contaminants in soil are available, none attempts to describe the combined effects of diffusion, adsorption and reaction for the Pb-contaminated soil system. The principal objectives of this work are to develop mathematical models which can be used to examine the fate of contaminants in the aggregate and continuous phase in the soil bed. The results obtained from the simulation of the models will be useful for identifying the most suitable treatment scheme for in situ stabilization. In the presentation which follows the remediation option considered is in situ stabilization.

## 2. Modeling and simulation of remediation of soil aggregates

### 2.1. Model development

Most soils have a variety of structural and textural heterogeneities that can significantly affect solute transport by creating different water flow velocities, and thus different solute concentrations within the soil [25]. Such kind of phenomenon is usually referred to as “preferential flow”, and it limits our ability to predict solute movement reliably using traditional mathematical models, such as the advection–dispersion equation.

In order to describe solute transport in soils where preferential flow occurs, a two-domain approach is often used [13,26]. With such an approach, the soil is conceptually divided into

two regions, one associated with the fraction of the soil that is highly permeable and the other with the less permeable pore system of the soil matrix. As a further simplification, water in the less permeable region is often regarded as immobile. For convenience, we will refer to the less permeable region as “aggregates”.

Solute transport in the preferential flow path is usually through advection, while for the aggregates diffusive exchange with the flow paths and within aggregates is important. If there is any reaction taking place between the solute and aggregate, it also accounts for solute transport.

A contaminated aggregates remediation model has been developed to describe the distribution of HA and newly produced pyromorphite in a single spherical aggregate surrounded by a HA dissolved solution. The impacts of initial concentration, diffusion coefficient, and aggregate size on the remediation time are assessed by numerically simulating the dynamic behavior of the in situ remediation process.

The remediation process is conceptualized as occurring in a system of porous, homogeneous spherical soil aggregates immersed in an aqueous solution of dissolved HA. The model considers that the lead contaminants are initially deposited uniformly in the soil aggregate. The HA diffuses into the aggregate and reacts with lead, which results in the production of pyromorphite. At the exterior surface of the particle, film diffusion controls the movement of species in and out of the bulk solution. Because the process is assumed to take place in a well-mixed system, diffusion within the bulk solution is ignored.

The following major assumptions are made in deriving the model for remediation in a soil aggregate.

1. Aggregates are in spherical shape.
2. Aggregates are saturated, homogeneous and isotropic and are made up of solid particles and stagnant water.
3. The temperature is constant in the aggregate.
4. Lead contaminants are uniformly deposited within the aggregate.
5. Reaction takes place in the pores and at solid surfaces within the aggregate.
6. The reaction is of first order with respect to HA and zero order with respect to lead.
7. Transport in the aggregate is by diffusion only, the rate of diffusion is retarded because of the tortuosity within the pores.
8. The transport resistance of HA to the solid particle surface is negligible.
9. The HA concentration at the aggregate surface is constant.
10. The initial amount of HA in solid phase is negligible.
11. The lead exists in phase equilibrium with liquid and solid phases; the diffusion of dissolved lead can be neglected.
12. No product layer will be formed on the solid particle, thus the lead within the aggregate is always accessible to the HA.

The mass balance for HA in a spherical aggregate gives rise to

$$4\pi r^2 \Delta r \varepsilon_a \frac{\partial c_A}{\partial t} = 4\pi \left( -r^2 \frac{D_A \varepsilon_a}{\tau} \frac{\partial c_A}{\partial r} \right) \Big|_r - 4\pi \left( -r^2 \frac{D_A \varepsilon_a}{\tau} \frac{\partial c_A}{\partial r} \right) \Big|_{r+\Delta r} + 4\pi r^2 \Delta r \varepsilon_a r_A \quad (1)$$

where subscript A stands for HA. Dividing both sides of Eq. (1) by  $4\pi r^2 \varepsilon_a$ , and taking the limit as  $\Delta r$  approaches 0 give

$$\frac{\partial c_A}{\partial t} = \frac{D_A}{\tau r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_A}{\partial r} \right) + r_A \quad (2)$$

The reaction rate equation is given by

$$r_A = -k_r c_A, \quad \text{if there is unreacted lead present} \quad (3)$$

$$r_A = 0, \quad \text{if there is no unreacted lead} \quad (4)$$

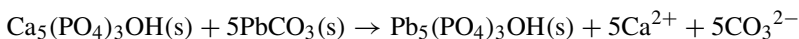
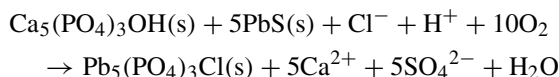
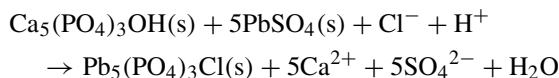
based on previous assumptions. The initial condition assumes there is no HA in the aggregate,  $t = 0$ ,  $c_A = 0$  for all  $r$ , while at the aggregate surface,  $c_A = c_A^0$  for all  $t$ . At  $r = 0$ ,

$$\frac{\partial c_A}{\partial r} = 0 \quad (5)$$

The rate of consumption of lead based on pyromorphite formation can be expressed as

$$-r_B = -5r_A = 5k_r c_A \quad (6)$$

based on the stoichiometry of the reaction



where subscript B represents lead compounds.

On the basis of unit mass, the rate of lead consumption can be expressed as

$$-\frac{dc_B}{dt} = \frac{-5000r_A \varepsilon_a M_B}{\rho} \quad (7)$$

The initial condition of this equation is at  $t = 0$ ,  $c_B = c_B^0$ .

The rate of pyromorphite formation can also be obtained based on the stoichiometry of the reaction.

$$r_P = -r_A = k_r c_A \quad (8)$$

where subscript P stands for pyromorphite.

On the basis of unit mass, Eq. (8) can be rewritten as

$$\frac{dc_P}{dt} = \frac{-1000r_A \varepsilon_a M_P}{\rho} \quad (9)$$

The initial condition of Eq. (8) at  $t = 0$  is  $c_P = 0$ .

## 2.2. Simulation

The governing equations of the model, Eqs. (2), (7) and (9) have been solved numerically. Three lead compounds ( $\text{PbSO}_4$ ,  $\text{PbCO}_3$  and  $\text{PbS}$ ) are investigated. For each lead compound, the effects of four parameters, which are the diffusion coefficient of HA, reaction rate constant, size of the aggregate and initial HA concentration, on the total remediation time are examined. Moreover, the initial lead concentration in the aggregate varies from 100 to 10,000 mg/kg for each case.

## 2.3. Results and discussion

The results of simulation for remediation of soil aggregates are presented Figs. 1–11. The points shown are simulation results, the points are used to distinguish one curve from another. Fig. 1 shows the effect of diffusion coefficient and initial contaminant concentration on the in situ stabilization time. Increasing the diffusion coefficient enhances transport of HA inside the aggregate which reduces remediation time greatly. Larger initial concentrations of contaminant require more HA which results in larger remediation time. The effect of diffusion coefficient is more significant at high initial contaminant concentration. Fig. 2 indicates that the reaction constant is also an important factor that affects the remediation process. The rate of conversion depends on the values of the rate constant as well as the diffusivity. Substantial increases in conversion time occur when either value is reduced.

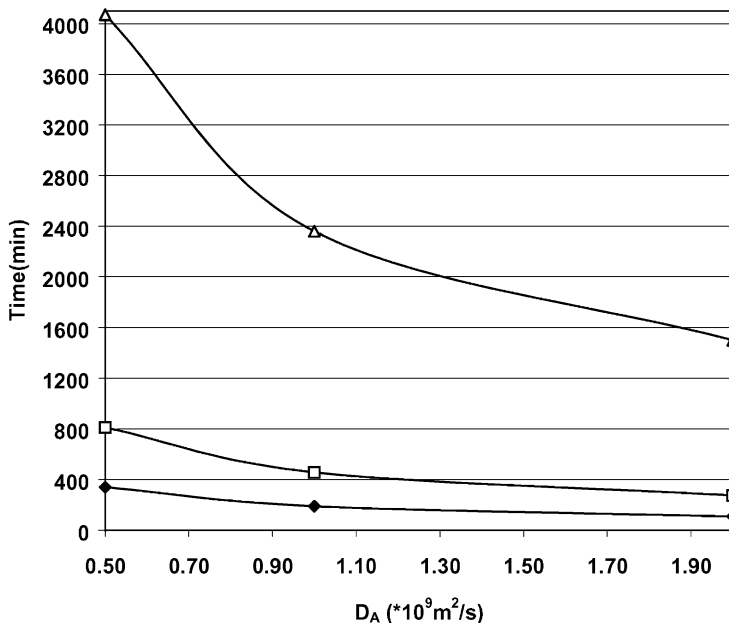


Fig. 1. Total conversion time for  $\text{PbCO}_3$  at different  $D_A$  ( $D_i = 0.02 \text{ m}$ ,  $c_A^0 = 2.6 \text{ kg/m}^3$ ,  $k_r = 10^{-4} \text{ l/s}$ ). (◆)  $c_B^0 = 100 \text{ mg/kg}$ ; (□)  $c_B^0 = 1000 \text{ mg/kg}$ ; (△)  $c_B^0 = 10,000 \text{ mg/kg}$ .

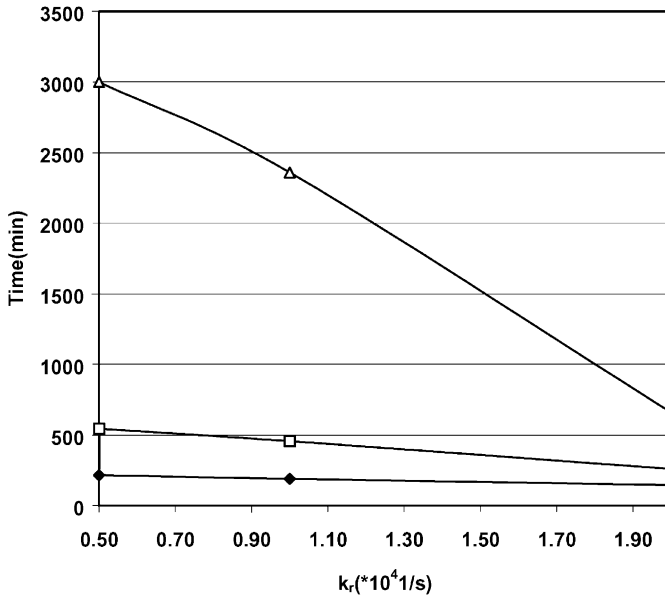


Fig. 2. Total conversion time for  $PbCO_3$  at different values of reaction rate constant ( $D_i = 0.02$  m,  $c_A^0 = 2.6$  kg/m<sup>3</sup>,  $D_A = 10^{-9}$  m<sup>2</sup>/s). ( $\blacklozenge$ )  $c_B^0 = 100$  mg/kg; ( $\square$ )  $c_B^0 = 1000$  mg/kg; ( $\Delta$ )  $c_B^0 = 10,000$  mg/kg.

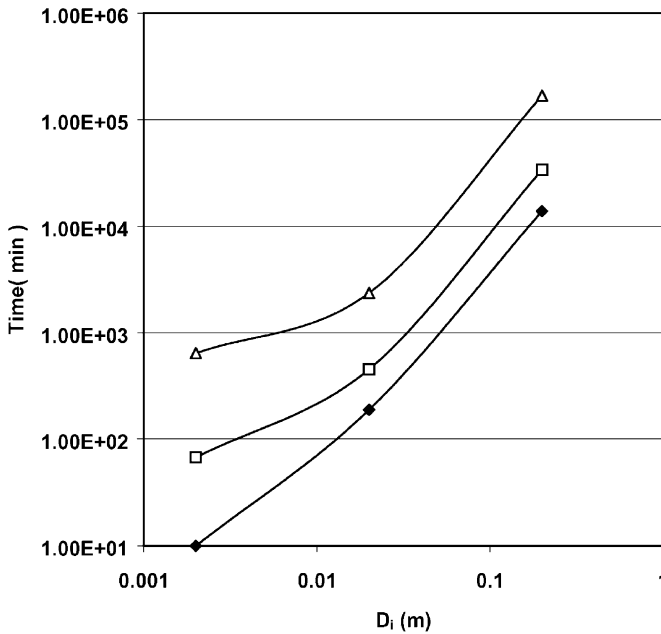


Fig. 3. Total conversion time for  $PbCO_3$  at different sizes of aggregates ( $k_r = 10^{-4}$  l/s,  $c_A^0 = 2.6$  kg/m<sup>3</sup>,  $D_A = 10^{-9}$  m<sup>2</sup>/s). ( $\blacklozenge$ )  $c_B^0 = 100$  mg/kg; ( $\square$ )  $c_B^0 = 1000$  mg/kg; ( $\Delta$ )  $c_B^0 = 10,000$  mg/kg.



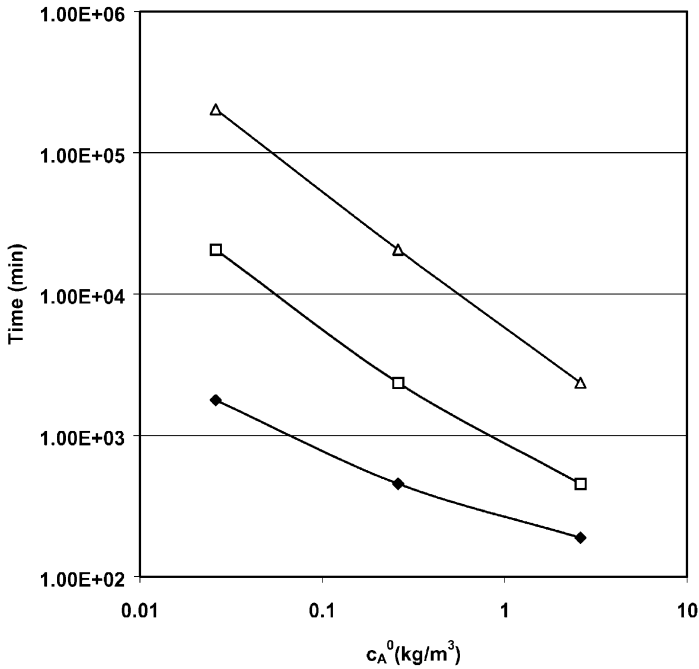


Fig. 4. Total conversion time for  $\text{PbCO}_3$  at different bulk hydroxyapatite concentrations ( $k_r = 10^{-4}$  l/s,  $D_i = 0.02$  m,  $D_A = 10^{-9}$  m<sup>2</sup>/s). (◆)  $c_B^0 = 100$  mg/kg; (□)  $c_B^0 = 1000$  mg/kg; (△)  $c_B^0 = 10,000$  mg/kg.

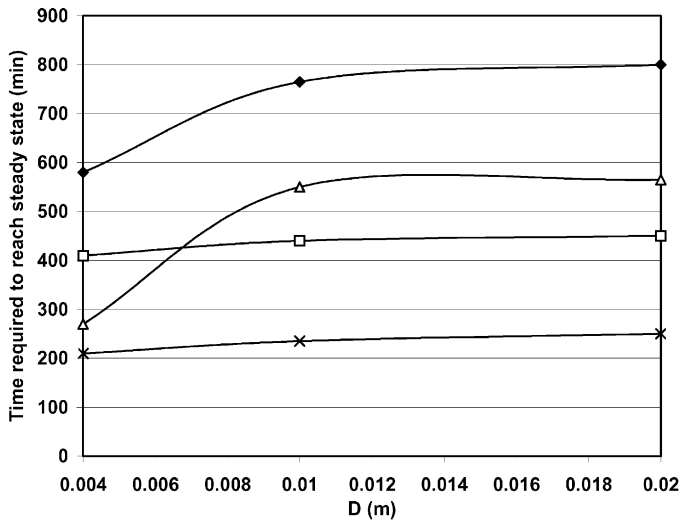


Fig. 5. Time required to reach a steady state hydroxyapatite concentration in the mobile liquid for  $\text{PbCO}_3$  at different values of  $D$  for selected values of mean fluid residence time,  $t_R$  and diffusivity,  $D_A$  (one compartment model). (◆)  $t_R = 69.4$  min,  $D_A = 10^{-9}$  m<sup>2</sup>/s; (□)  $t_R = 69.4$  min,  $D_A = 10^{-8}$  m<sup>2</sup>/s; (△)  $t_R = 34.7$  min,  $D_A = 10^{-9}$  m<sup>2</sup>/s; (×)  $t_R = 34.7$  min,  $D_A = 10^{-8}$  m<sup>2</sup>/s.

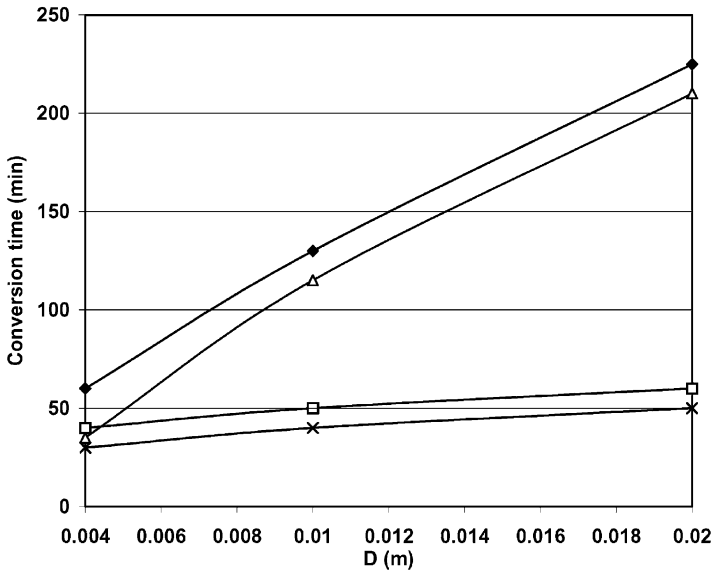


Fig. 6. Total remediation time for  $PbCO_3$  at different values of  $D$  for selected values of mean fluid residence time,  $t_R$  and diffusivity,  $D_A$  (one compartment model). (◆)  $t_R = 69.4$  min,  $D_A = 10^{-9}$  m<sup>2</sup>/s; (□)  $t_R = 69.4$  min,  $D_A = 10^{-8}$  m<sup>2</sup>/s; (△)  $t_R = 34.7$  min,  $D_A = 10^{-9}$  m<sup>2</sup>/s; (×)  $t_R = 34.7$  min,  $D_A = 10^{-8}$  m<sup>2</sup>/s.

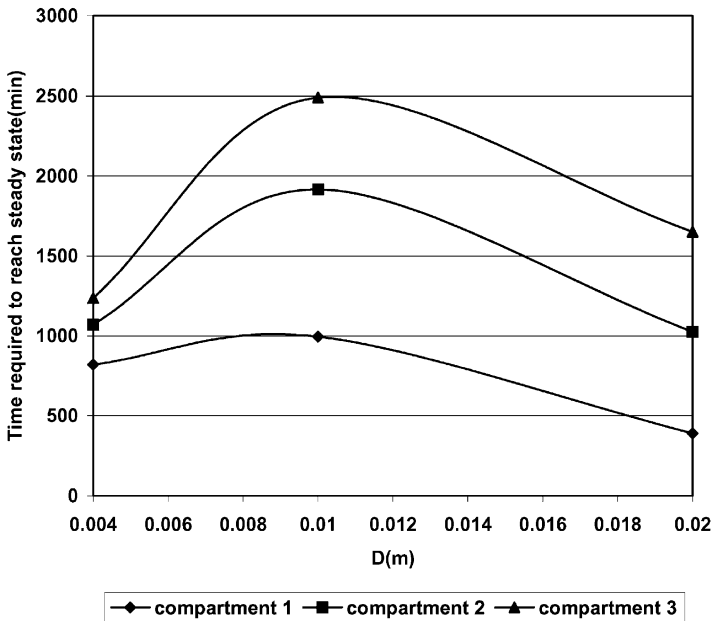


Fig. 7. Time required to reach a steady state hydroxyapatite concentration in the mobile liquid for  $PbCO_3$  at different values of  $D$  ( $t_R = 69.4$  min,  $D_A = 10^{-10}$  m<sup>2</sup>/s) (three compartments-in-series model).

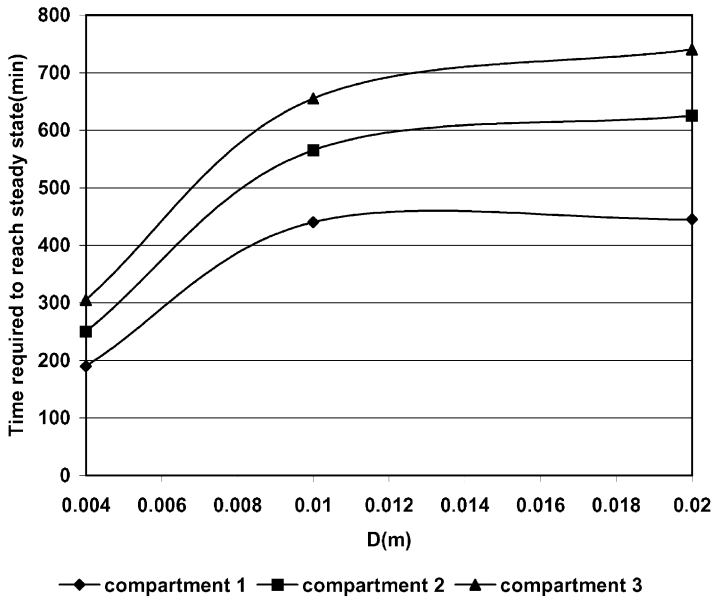


Fig. 8. Time required to reach a steady state hydroxyapatite concentration in the mobile liquid for  $\text{PbCO}_3$  at different values of  $D$  ( $t_R = 69.4$  min,  $D_A = 10^{-9}$  m<sup>2</sup>/s) (three compartments-in-series model).

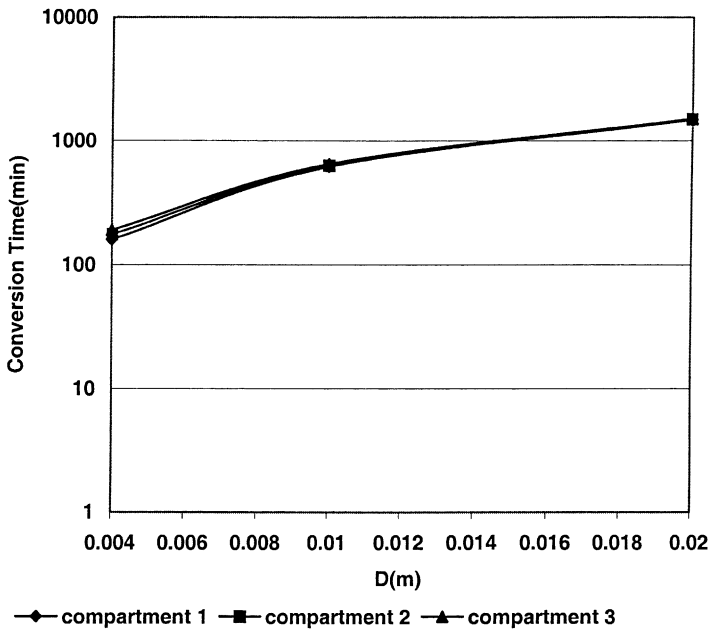


Fig. 9. Total conversion time for  $\text{PbCO}_3$  at different values of  $D$  for  $t_R = 69.4$  min and  $D_A = 10^{-10}$  m<sup>2</sup>/s (three compartments-in-series model).

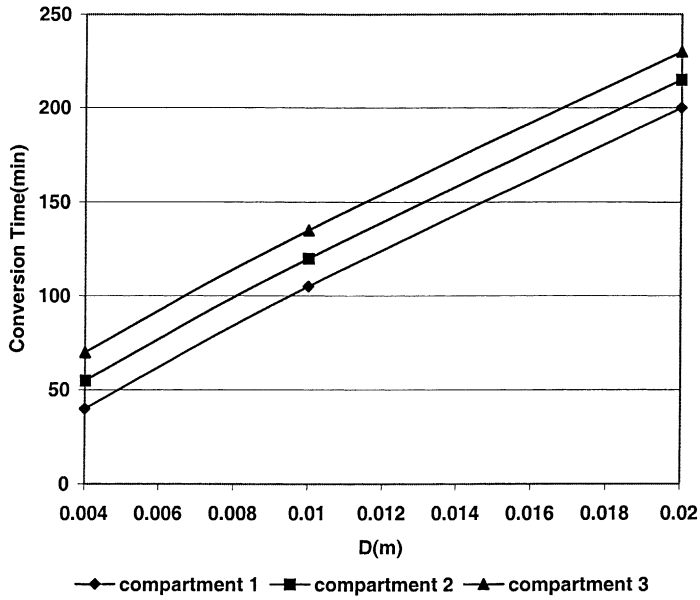


Fig. 10. Total conversion time for  $\text{PbCO}_3$  at different values of  $D$  (three compartments-in-series model)  $t_R = 69.4$  min,  $D_A = 10^{-9}$  m<sup>2</sup>/s.

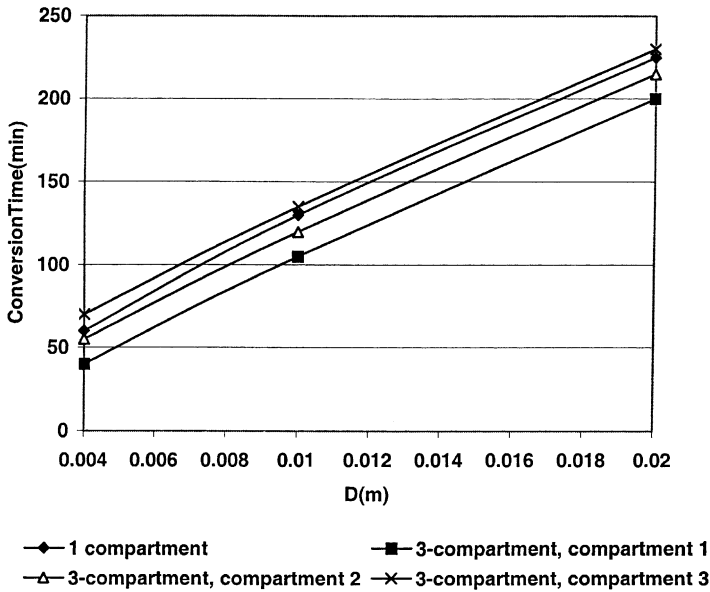


Fig. 11. Total conversion time for  $\text{PbCO}_3$  at different values of  $D$  for  $t_R = 34.7$  min and  $D_A = 10^{-9}$  m<sup>2</sup>/s (one compartment vs. three compartment).

The effect of reaction rate constant is also more significant at high initial contaminant concentration. Fig. 3 reveals the effect of aggregate size on the remediation time. For aggregates with small diameter, the HA diffuses more rapidly inside the aggregates. The HA moves extremely slow in large aggregates, which causes longer remediation time. Fig. 4 indicates that the concentration of HA affects significantly the time of remediation. Large HA concentration makes HA more accessible to react with lead contaminant which leads to shorter remediation time compared with small HA concentrations. Since HA solubility is higher at low pH (Table 1), it is necessary to consider the effects of pH on solubility in Fig. 4. The aqueous phase concentration of HA can not exceed the solubility of HA in water. The remediation time is defined as the time needed for the concentration of lead contaminant in the aqueous phase to drop below 1 ppb.

### 3. Modeling and simulation of remediation of soil bed with a compartments-in-series model

#### 3.1. Model development

The macropore flow in a contaminated soil bed can be adequately described by a plug flow model if the dispersion effects are negligible or very small. However, a plug flow model for an aggregated bed is very difficult to construct because of mathematical complexities involved in making the appropriate mass balances for the aggregates and maintaining the macropore continuum. In this section, a compartments-in-series model has been developed and simulated to investigate the fate of contaminants in the soil bed. Results for three compartments-in-series have been compared with the single compartment case.

The model in this section considers the influence of intra-aggregate micropore diffusion in addition to the inter-aggregate macropore flow in the soil bed. The mass transport within the aggregate results from both diffusion and reaction inside the aggregate. The mass transport in the macropores is convective and is assumed to be completely mixed in each compartment.

The following assumptions are made in deriving this model.

1. The soil bed is divided into equal-volume, well-mixed compartments in series.
2. The bed is composed of spherical soil aggregates of a uniform size.
3. The aggregates are saturated, homogenous and isotropic and are made up of solid particles and stagnant water.
4. The temperature is constant in the bed.
5. The reaction rate within the aggregates follows  $r_A = -kc_A$  (subscript A denotes hydroxyapatite).
6. Lead contaminant is uniformly deposited within the aggregate.
7. Transport in the aggregate is by diffusion only.
8. The transport resistance of HA to the solid particle surface is negligible.
9. The mobile liquid in the macropores of the bed is completely mixed within each compartment; thus, the concentration of HA leaving the soil bed is equal to that in the macropores of the bed of the compartment.

The material balance equations are derived as follows: first, the material balance equation for the mobile phase in the macrovoids of the bed is derived by taking the mass balance of HA in the liquid phase, which gives rise to

$$\varepsilon_1 V \frac{dc_{A,ml}^j}{dt} = Q(c_{A,ml}^{j-1} - c_{A,ml}^j) - VaJ_A \quad (10)$$

The interfacial area of the aggregates per unit volume of the bed,  $a$ , is written as

$$a = \frac{3}{R}(1 - \varepsilon_1) \quad (11)$$

The rate of mass transfer of HA at the surface of the aggregates is expressed as

$$J_A = -\varepsilon_a D_{A,pl} \left. \frac{\partial c_{A,pl}^j}{\partial r} \right|_{r=R} \quad (12)$$

Substituting the above mass transfer expression, Eq. (12) and the interfacial area term, Eq. (11) into Eq. (10) gives rise to

$$\varepsilon_1 V \frac{dc_{A,ml}^j}{dt} = Q(c_{A,ml}^{j-1} - c_{A,ml}^j) - \frac{3}{R}(1 - \varepsilon_1)V\varepsilon_a D_{A,pl} \left. \frac{\partial c_{A,pl}^j}{\partial r} \right|_{r=R} \quad (13)$$

This is the general equation for HA in the mobile liquid phase in the macrovoids of the soil bed, where subscript A, ml, pl stands for HA, mobile liquid and pore liquid, respectively;  $\varepsilon_1$ ,  $\varepsilon_a$  the macrovoid fraction of the bed and the void fraction of microvoid in the aggregate respectively; and  $Q$ , the volumetric flow rate of liquid into the bed. The superscript  $j$  denotes the  $j$ th bed.

The mass balance for HA in a spherical aggregate gives rise to

$$4\pi r^2 \Delta r \varepsilon_a \frac{\partial c_A^j}{\partial t} = 4\pi \left( -r^2 \frac{D_A \varepsilon_a}{\tau} \frac{\partial c_A^j}{\partial r} \right) \Big|_r - 4\pi \left( -r^2 \frac{D_A \varepsilon_a}{\tau} \frac{\partial c_A^j}{\partial r} \right) \Big|_{r+\Delta r} + 4\pi r^2 \Delta r \varepsilon_a r_A^j \quad (14)$$

where subscript A stands for hydroxyapatite (HA). Dividing both sides of Eq. (14) by  $4\pi r^2 \varepsilon_a$ , and taking the limit as  $\Delta r$  approaches 0 give

$$\frac{\partial c_A^j}{\partial t} = \frac{D_A}{\tau r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_A^j}{\partial r} \right) + r_A^j \quad (15)$$

The reaction rate equation is given by

$$r_A^j = -k_r c_A^j, \quad \text{if there is unreacted lead present} \quad (16)$$

$$r_A = 0, \quad \text{if there is no unreacted lead} \quad (17)$$

The initial condition is there is no HA in the aggregate and mobile liquid,  $t = 0$ ,  $c_{A,pl}^j = 0$  for all  $r$  and  $c_{A,ml}^j = 0$ , while at the aggregate surface,  $c_{A,pl}^j = c_{A,ml}^j$  for all  $t > 0$ . At  $r = 0$ ,

$$\frac{\partial c_{A,pl}^j}{\partial r} = 0 \quad (18)$$

The diffusion of lead in the solid phase is negligible, hence the rate of consumption of lead based on pyromorphite formation can be expressed as

$$-r_B^j = -5r_A^j = 5k_r c_A^j \quad (19)$$

based on the stoichiometry of the reactions, which appear in the previous section.

On the basis of unit mass, the rate of lead consumption is

$$-\frac{dc_B^j}{dt} = \frac{-5000r_A^j \varepsilon_a M_B}{\rho} \quad (20)$$

The initial condition of this equation is at  $t = 0$ ,  $c_B^j = c_B^{j0}$ . The rate of pyromorphite formation can also be obtained based on the stoichiometry of the reaction.

$$r_P^j = -r_A^j = k_r c_A^j \quad (21)$$

where subscript P stands for pyromorphite. On the basis of unit mass, Eq. (21) can be rewritten as

$$\frac{dc_P^j}{dt} = \frac{-1000r_A^j \varepsilon_a M_P}{\rho} \quad (22)$$

The initial condition of Eq. (22) at  $t = 0$  is  $c_P^j = 0$ .

### 3.2. Simulation

The soil bed is assumed to contain  $N$  compartments. The system is described by  $3N$  coupled ODEs, Eqs. (10), (20) and (22),  $j = 1, \dots, N$ , and  $NP$ DEs, Eq. (15),  $j = 1, \dots, N$ . In this study, we compare a single compartment with three compartments-in-series; thus,  $N$  is equal to 1 or 3. All the equations are solved numerically.  $PbCO_3$  is investigated as the lead contaminant. The effects of aggregate size, diffusion coefficient of HA and mean fluid residence time on the total remediation time are examined. Comparison between one compartment and three compartments-in-series has been made based on the simulation results.

### 3.3. Results and discussion

The results have been obtained by simulating the dynamics of in situ stabilization in the soil bed. For all the simulations, the concentration of lead contaminant is 100 mg/kg; reaction rate constant  $k$  is assumed to be  $10^{-4}/s$ ; entering concentration of HA  $c_A^0$  equals to

2.6 kg/m<sup>3</sup>;  $\varepsilon_1$  and  $\varepsilon_a$  are both 0.5. The sensitivity analysis has been performed to describe the effects of diffusion coefficient, aggregate radius, and liquid phase mean residence time on the remediation time. The simulation is terminated when the contaminant concentration drops below 1 ppb everywhere within the soil bed, subsequently, the remediation time (conversion time) is determined. Time required to reach steady state in the mobile phase is defined as the time required for the concentration of HA in the macropore to reach 99% of the initial feed concentration.

Simulation results are presented in Figs. 5–11. Figs. 5 and 6 summarize the effects of both mean fluid residence time and diffusion coefficient on the time required to convert lead carbonate to lead pyromorphite and establish a steady state HA concentration. For small aggregate size, the effect of mean fluid residence time is more significant than that of diffusion coefficient. As shown in Fig. 6, the diffusion coefficient has a significant effect on the total remediation time when aggregate diameter is over 0.004 m. Meanwhile, as the size of the aggregate increases and the diffusion coefficient decreases, or equivalently, the Thiele modulus, which is defined as [27]

$$M_T = \frac{D}{6} \sqrt{\frac{k}{D_A}}, \quad \text{for spherical particle} \quad (23)$$

where  $D$  is the diameter of the aggregate,  $k$  the reaction rate constant, and  $D_A$  the diffusion coefficient of HA, increases, it is observed that the total conversion time increases dramatically. This is because the HA concentration drops rapidly toward zero on moving into the micropore of the aggregate, hence diffusion strongly influences the rate of reaction. In the regime of strong pore resistance, changing mean fluid residence time, or equivalently, the flow rate of HA will not affect the conversion time very much, which can be seen from Fig. 6.

Figs. 7–11 present the simulation results for the three compartments-in-series model. As shown in Fig. 9 the remediation time for the different compartments is almost the same when the diffusion coefficient is at  $10^{-10}$  m<sup>2</sup>/s. For the values of mean fluid residence time selected for this work, the diffusion into the aggregates is limiting for  $D_A = 10^{-10}$  m<sup>2</sup>/s. Thus, the results are nearly identical to those in Fig. 9 for a range of mean residence times. Comparison of Figs. 7 and 9 shows that for the first compartment, the remediation time for larger aggregates in Fig. 9 is larger than the time required to reach a steady state HA concentration in the mobile phase as shown in Fig. 7. This implies that the rate of diffusion into the larger aggregate is small compared to the rate at which HA is supplied to the mobile phase of the compartment. When the value of the diffusivity is increased to  $10^{-9}$  m<sup>2</sup>/s, the remediation time is smaller than the time required to reach a steady state HA concentration in the mobile phase, which is shown by comparison of Figs. 8 and 10. Fig. 11 reveals that for the total bed volume, a single well-mixed, one compartment model gives approximately the same remediation time in comparison with three compartments-in-series model.

#### 4. Discussion and conclusions

In the soil aggregate model, the diffusion resistance within the aggregate alone is taken into account. In the real system, both resistances at the aggregate surface and within the



aggregate are important and should be considered simultaneously, which may result in longer remediation times for many systems. In the case of large aggregates, the time to remediate them using apatite is much less than the time for contaminants to diffuse out of the aggregates. Under diffusion controlled conditions, treatment in which bigger aggregates are broken up into smaller ones could be employed for faster cleanup. The compartments-in-series model has been used to describe the dynamics of remediation in soil bed. The comparison of results for three compartments-in-series with those for a single compartment model has demonstrated that for a small bed, where the diffusion into the aggregates is rate controlling, the dynamics of remediation may be described by a compartments-in-series model or a single completely mixed compartment without much difference in the remediation time or concentration profiles in the macropores. These models can be used to estimate the time required for in situ stabilization for a range of environmental conditions.

Results are presented for  $\text{PbCO}_3$  in this work. Similar results have been obtained for  $\text{PbSO}_4$  and  $\text{PbS}$  [28].

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