

# MODEL DEVELOPMENT AND SIMULATION OF *IN SITU* STABILIZATION IN LEAD-CONTAMINATED SOILS

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## ABSTRACT

Stabilization and remediation of lead-contaminated soils have 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 the present work, models which include adsorption, diffusion, and reaction have been developed to describe the transformation of lead contaminants to pyromorphite in single particles, aggregates, and soil beds, respectively. Principal factors controlling the time of remediation have been identified.

The contaminated aggregates remediation model has been developed and simulated to describe the effect of initial contaminant concentration, diffusion coefficient, and aggregate diameter on the time of remediation.

**Key words:** modeling, stabilization, remediation, hydroxyapatite, lead pyromorphite, bioavailability

## INTRODUCTION

*In situ* stabilization of soil lead by the addition of phosphate minerals has been considered a cost-effective and environmentally benign alternative remediation technology for Pb-contaminated soils. This method transforms the reactive and bioavailable Pb into chemical forms that are stable and have extremely low solubility, mobility, and bioavailability under typical environmental conditions.

Lead pyromorphite is one of the most stable Pb forms in soils under a wide variety of environmental conditions. (Lindsay, 1979). Ma et al. (1993) showed that hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) has the potential of immobilizing Pb in solution by forming hydroxypyromorphite. Formation of pyromorphites upon addition of apatite or soluble inorganic P amendments has been observed in

Pb-contaminated soil materials. (Cotter-Howells and Caporn, 1996).

However, little attention has been paid to modeling the formation of pyromorphite using mathematical methods. In this study, models are developed for both single-particle and soil aggregates. Furthermore, two cases, stagnant surroundings and flowing surroundings, are considered with respect to the single particle.

## MODEL DEVELOPMENT FOR A SINGLE PARTICLE

First, consider the case where all lead in the particle is in the process of being completely converted to pyromorphite. *A* (hydroxyapatite) must diffuse to the surface to react with solid *B* (lead compound) at the liquid-solid surface. Reactions of this type are typically zero order in *B* and first order in *A* ( $r = -k_r c_A$  when  $C_B > 0$  and

$r = 0$  when  $C_B = 0$ ). The rate of the mass transfer to the surface is equal to the rate of surface reaction.

The following assumptions are imposed while deriving the model:

- (1) Particles are in spherical form.
- (2) Reaction only takes place at the solid-liquid surface.
- (3) The product does not form a layer on the particle. The unreacted part of the particles is always accessible to the hydroxyapatite.
- (4) The concentration of the hydroxyapatite is kept constant. The rate of consumption of hydroxyapatite is

$$W_{Ar} = k_c(c_A - c_{As}) = -r_A = k_r c_{As} \quad (1)$$

Eliminating the surface concentration of A,  $c_{As}$ , gives

$$W_{Ar} = -r_A = \frac{k_c k_r}{k_c + k_r} c_A \quad (2)$$

We consider two cases:

- (1) The particle is immersed in a stagnant fluid, in which case the Sherwood number is

$$Sh = \frac{k_c D}{D_A} = 2 \quad (3)$$

- (2) The fluid flows around the particle, in which case

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (4)$$

where

$$Re = \frac{DU}{\nu}$$

$$Sc = \frac{\nu}{D_A}$$

### Case 1: Stagnant Fluid

From Equation(3), the mass transfer

coefficient is

$$k_c = \frac{2D_A}{D} \quad (5)$$

Equation (2) may be written as

$$-r_A = \frac{k_c k_r}{k_c + k_r} c_A = \frac{k_r}{1 + k_r/k_c} c_A \quad (6)$$

Substituting Equation (5) into the above equation gives

$$-r_A = \frac{k_r}{1 + \frac{k_r D}{2D_A}} c_A = \frac{k_r c_A}{1 + D/D^*} \quad (7)$$

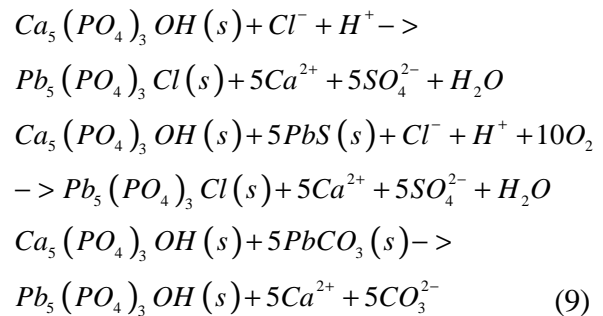
where  $D^* = 2D_A/k_r$

A lead mole balance on the solid particles yields

In – Out + Generation = Accumulation

$$0 - 0 + r_B \pi D^2 = \frac{d(\rho \pi D^3/6)}{dt} \quad (8)$$

According to the stoichiometric relation of A and B, lead pyromorphite can be formed with either chloride or hydroxyl ions:



For all cases, we have:  $-5r_A = -r_B$

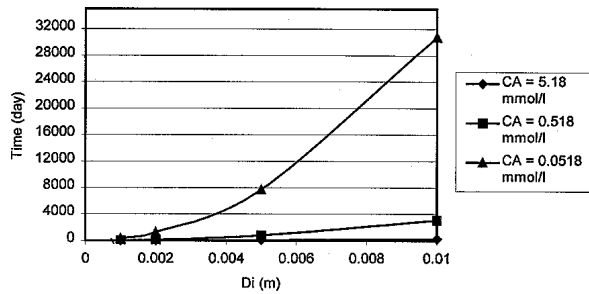
Equations (7), (8) and (9) can be used to obtain

$$\frac{dD}{dt} = -\frac{10(-r_A)}{\rho} = -\frac{10k_r c_A}{\rho} \frac{1}{1 + D/D^*}$$

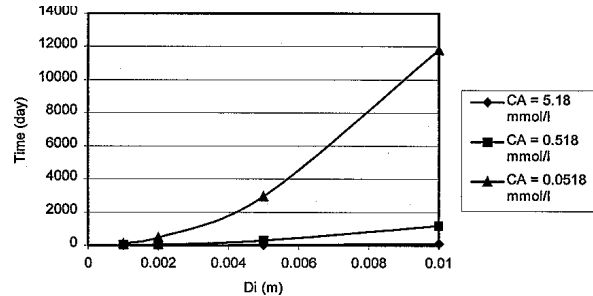
$$\frac{dD}{dt} = -\alpha \frac{1}{1 + D/D^*} \quad (10)$$

where

$$\alpha = \frac{10k_r c_A}{\rho} \quad (11)$$



**Figure 1.** Conversion time for lead for the case of a static aqueous phase.



**Figure 2.** Conversion time for PbSO<sub>4</sub> for the case of a static aqueous phase.

At  $t=0, D=D_i$

Equation (11) can be integrated to obtain

$$D_i - D + \frac{1}{2D^*} (D_i^2 - D^2) = \alpha t$$

The time for complete conversion is found by letting  $D=0$ ; that is,

$$t_c = \frac{1}{\alpha} \left( D_i + \frac{D_i^2}{2D^*} \right) \quad (12)$$

Consider four different species of B:

- (1) Pb  $\rho = 5.48 * 10^4 \text{ mol/m}^3$
- (2) PbSO<sub>4</sub>  $\rho = 2.10 * 10^4 \text{ mol/m}^3$
- (3) PbCO<sub>3</sub>  $\rho = 2.45 * 10^4 \text{ mol/m}^3$
- (4) PbS  $\rho = 3.17 * 10^4 \text{ mol/m}^3$

Three different concentration of hydroxyapatite:

$$c_A = 5.18 \text{ mol/m}^3$$

$$c_A = 0.518 \text{ mol/m}^3$$

$$c_A = 0.0518 \text{ mol/m}^3$$

Four different initial particle diameters:

$$D_i = 0.001 \text{ m}$$

$$D_i = 0.002 \text{ m}$$

$$D_i = 0.005 \text{ m}$$

$$D_i = 0.01 \text{ m}$$

Let  $k_r = 10^{-4} \text{ m/s}$ ,  $D_A = 10^{-9} \text{ m}^2/\text{s}$ .

The results for this case are shown on Figures 1-4.

### Case 2: Flowing Fluid

In this case

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad (3)$$

in which

$$Sc = \frac{\nu}{D_A} = \frac{10^{-6} \text{ m}^2/\text{s}}{10^{-9} \text{ m}^2/\text{s}} = 1000$$

$$Re = \frac{DU}{\nu} = \frac{D * U \text{ m/s}}{10^{-6} \text{ m}^2/\text{s}} = 10^6 DU$$

(take fluid velocity as U m/s)

$$Sh = \frac{k_c D}{D_A} = 2 + 0.6 * (10^6 DU)^{1/2} (1000)^{1/3}$$

$$= 2 + 6000 \sqrt{DU}$$

$$\text{Then } k_c = \frac{(2 + 6000 \sqrt{DU}) * D_A}{D} \quad (13)$$

From (6)

$$-r_A = \frac{k_r}{1 + k_r/k_c} c_A$$

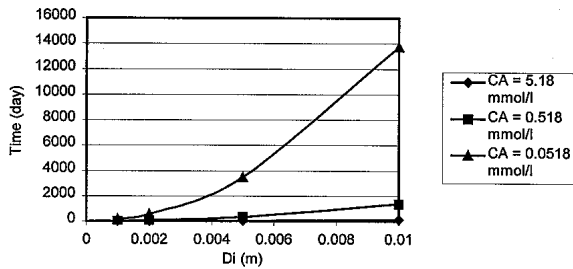
Substituting Equation (13) into Equation

(6) we have

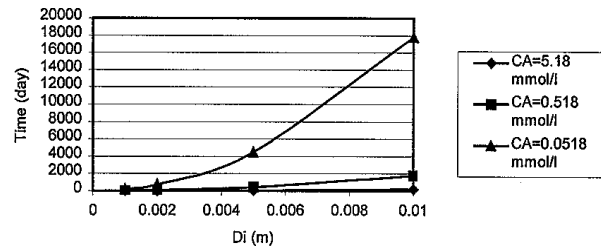
$$-r_A = \frac{k_r}{1 + k_r/k_c} c_A = \frac{k_r c_A}{1 + \frac{k_r D}{(2 + 6000 \sqrt{DU}) * D_A}}$$

Again

$$\frac{dD}{dt} = -\frac{10(-r_A)}{\rho} = -\frac{10k_r c_A}{\rho} *$$



**Figure 3.** Conversion time for  $\text{PbCO}_3$  for the case of a static aqueous phase.



**Figure 4.** Conversion time for  $\text{PbS}$  for the case of a static aqueous phase.

$$1 + \frac{k_r D}{(2 + 6000\sqrt{DU}) * D_A}$$

$$= -\alpha \frac{1}{1 + \frac{k_r D}{(2 + 6000\sqrt{DU}) * D_A}}$$

where,

$$\alpha = -\frac{10k_r c_A}{\rho}$$

$$\frac{dD}{dt} = -\alpha \frac{(2 + 6000\sqrt{DU}) * D_A}{(2 + 6000\sqrt{DU}) * D_A + k_r D} \quad (14)$$

Numerical methods are used to solve this differential equation.

The results for this case are given by Figures 5-8.

## DISCUSSION OF RESULTS

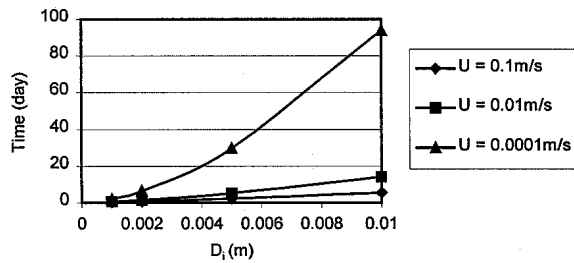
### *Simulation for lead particle in stagnant fluid*

The results of simulation for the case of a single lead particle surrounded by a stagnant fluid are presented in Figures 1 through 4. In Figure 1, three different concentrations of the applied hydroxyapatite and particles with four different diameters are considered. The results indicate that the concentration of hydroxyapatite affects the time of remediation significantly. At

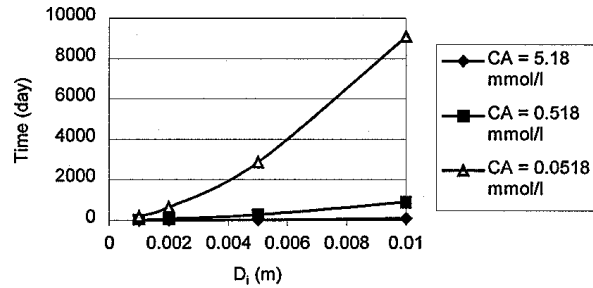
large hydroxyapatite concentrations, the remediation process takes place much faster compared with small hydroxyapatite concentrations, because the reaction rate is first order with respect to the concentration of hydroxyapatite. Also Figure 1 reveals the effect of particle diameter on the rate of remediation. For particles with small diameters, the hydroxyapatite diffuses more rapidly inside the particle. The hydroxyapatite moves extremely slow in large particles, thereby prolonging substantially the time for remediation. Figures 1 through 4 show that the initial lead concentration also has an effect on the remediation time. A small initial contaminant concentration requires a small hydroxyapatite supply. Thus less time is required for completion of the formation of pyromorphite.

### *Simulation of lead particle in flowing fluid*

The results of simulation for the case of a single lead particle surrounded by a flowing fluid are shown in Figures 5 through 8. Figure 5 indicates that the flow rate of the surrounding fluid has an effect on the remediation time. With larger flow rate, the mass transfer coefficient is greatly enlarged, which significantly enhances the remediation process. Comparison of Figure 1 with Figure 6 reveals that at the same condi-



**Figure 5.** Conversion time for lead with flowing surroundings at different flow velocities ( $D=10^{-9}$   $m^2/s$ ,  $k_r=10^{-4}$   $m/s$ ,  $c_A=5.15$   $mmol/l$ ).



**Figure 6.** Conversion time for Pb at different values of  $c_A$  ( $D_A=10^{-9}$   $m^2/s$ ,  $k_r=10^{-4}$   $m/s$ ,  $U=10^{-4}$   $m/s$ ).

tion, flowing surroundings will effectively reduce the remediation time, even at a low flow rate of  $U = 10^{-4}$   $m/s$ . Figures 6 and 8 also indicate that the concentration of hydroxyapatite has a great effect on the remediation process in the cases with flowing surroundings. Larger particles take more time to complete the process.

### CONTAMINATED AGGREGATE REMEDIATION MODEL

The contaminated aggregate remediation model considers that the lead contaminants are initially uniformly deposited in soil aggregates. The following assumptions are made in deriving the model:

- Aggregates are in spherical shape;
- Aggregates are saturated, homogeneous, and isotropic and are made up of solid particles and stagnant water;
- The temperature is constant in the aggregate;
- Lead contaminants are uniformly deposited within the aggregate;
- Reaction takes place at solid surfaces within the aggregate;
- The reaction is of 1<sup>st</sup> order with respect to HA and 0 order with respect to lead compound;

g. Transport in the aggregate is by diffusion only;

h. The transport resistance of HA to the solid particle surface is negligible;

i. The HA concentration at the aggregate surface is constant;

j. The initial amount of HA in solid phase is negligible;

k. The lead compound exists in phase equilibrium with liquid and solid phases; the diffusion of dissolved lead compound concentration can be neglected;

l. No product layer will be formed on the solid particle.

The mass balance of HA in a spherical aggregate gives

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

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

$$r_A = 0 \quad \text{if there is no unreacted lead}$$

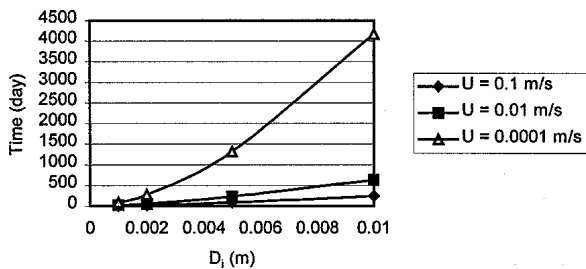
$$\text{I.C. } t = 0, c_A = 0 \quad \text{for all } r$$

$$\text{B.C. } c_A = c_A^0 \quad \text{at } r=R, \text{ for all } t$$

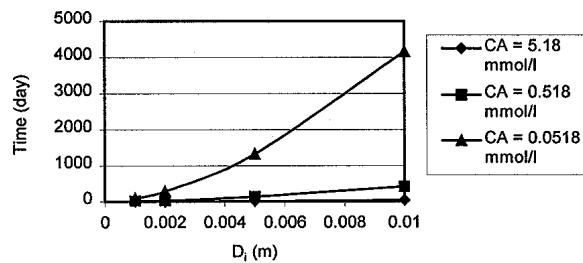
If the diffusion of lead is neglected,

$$-r_B = -5r_A = -5k_r c_A$$

$$\frac{dc_B}{dt} = -5r_A \epsilon / \rho * 10^6$$



**Figure 7.** Conversion time for  $\text{PbCO}_3$  ( $D_A=10^{-9} \text{ m}^2/\text{s}$ ,  $k_r=10^{-4} \text{ m/s}$ ,  $c_A=0.0518 \text{ mmol/l}$ ).



**Figure 8.** Conversion time for  $\text{PbCO}_3$  for different values of  $c_A$  ( $D_A=10^{-9} \text{ m}^2/\text{s}$ ,  $k_r=10^{-4} \text{ m/s}$ ,  $U=10^{-4} \text{ m/s}$ ).

$$\text{I.C. } t = 0, c_B = c_B^0$$

For pyromorphite,

$$r_p = -r_A = -k_r c_A$$

$$\frac{dc_p}{dt} = r_A \epsilon / \rho * 10^6$$

$$\text{I.C. } t = 0, c_p = 0$$

Numerical results are shown on Figures 9-14.

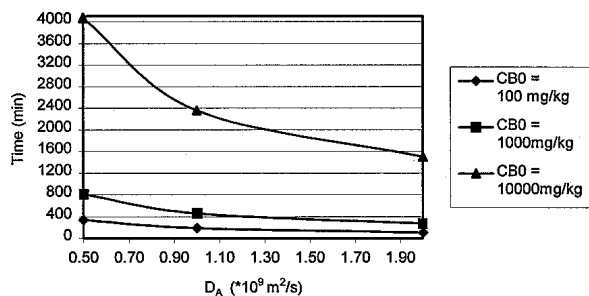
## DISCUSSION OF RESULTS

The results of simulation for remediation of soil aggregates are presented in Figures 9 through 14. Figure 9 shows the effect of diffusion coefficient and initial contaminant concentration on the remediation time. Increasing the diffusion coefficient enhances transport of hydroxyapatite inside the aggregate which reduces remediation time greatly. Larger initial concentrations of contaminant need more hydroxyapatite, which results in larger remediation time. The effect of diffusion coefficient is more significant at high initial contaminant concentration. Figure 10 indicates that reaction constant is also an important factor that affects the remediation process. Figures 9 and 10 show that 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. The

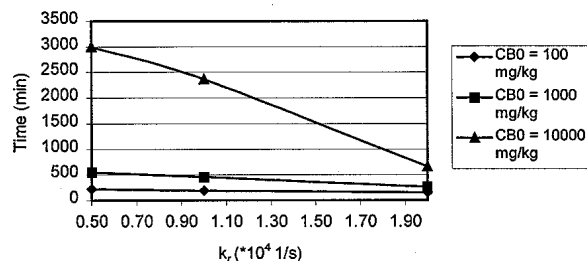
effect of reaction rate constant is also more significant at high initial contaminant concentration. Figure 11 reveals the effect of aggregate size on the rate of remediation. For aggregates with small diameter, the hydroxyapatite diffuses more rapidly inside the aggregates. The hydroxyapatite moves extremely slowly in large aggregates, which causes longer remediation time. Figure 12 indicates that the concentration of hydroxyapatite affects significantly the time of remediation. Large hydroxyapatite concentrations make hydroxyapatite more accessible to react with lead contaminants, which leads to shorter remediation times compared with small hydroxyapatite concentrations. Figure 13 shows that at the same condition,  $\text{PbS}$  is the most difficult to remediate because of its larger density among the three lead contaminants examined. Figure 14 presents a concentration profile at the center of the aggregate as a function of reaction time. The remediation time is defined as the time needed for the concentration of lead contaminant to drop below 1 ppb.

## CONCLUSION

Mathematical models have been developed to analyze lead stabilization in a single-soil particle and aggregated soil. In a single-soil



**Figure 9.** Total conversion time for  $\text{PbCO}_3$  for different values of  $D_A$  ( $D=0.02$  m,  $c_A^0=2.6$  g/l,  $k_r=10^{-4}$  1/s).



**Figure 10.** Total conversion time for  $\text{PbCO}_3$  at different value of reaction rate constant ( $D=0.02$  m,  $c_A^0=2.6$  g/l,  $D_A=10^{-9}$  m<sup>2</sup>/s).

particle model, only the diffusion resistance at the particle surface is considered. While in a soil-aggregate model, the diffusion resistance within the aggregate alone is taken into account. In the real system, both resistances are important and should be considered simultaneously, which may result in longer remediation time for the system.

#### ACKNOWLEDGEMENTS

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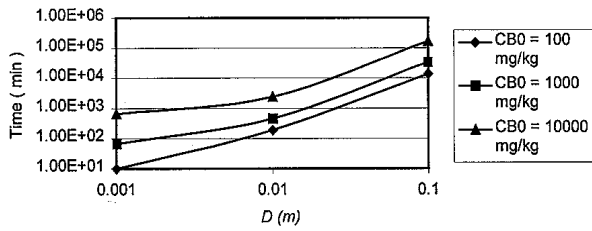
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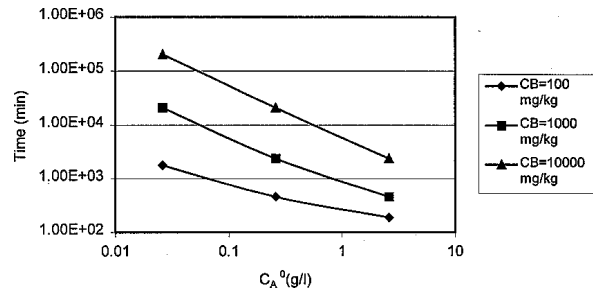
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#### NOTATION

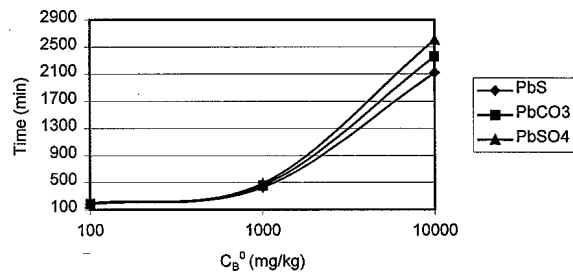
- $k_c$  mass transfer coefficient (m/s)
- $k_r$  reaction rate constant (m/s)
- $r_A$  rate of reaction of A (mol/m<sup>2</sup>s)
- $D_A$  effective diffusion coefficient (m<sup>2</sup>/s)
- $D_i$  initial diameter of the particle (m)
- $\rho$  density of the solid particle or aggregate (kg/m<sup>3</sup>)
- $\varepsilon$  volumetric fraction of liquid in the aggregate



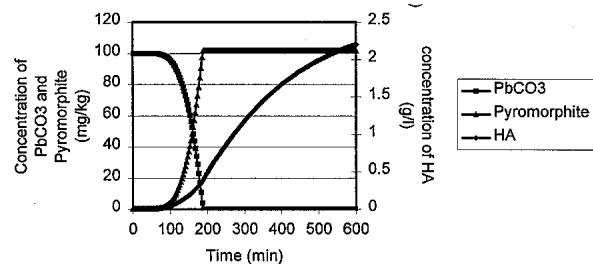
**Figure 11.** Total conversion time for  $\text{PbCO}_3$  at different diameters of aggregate ( $k_r=10^{-4}1/s$ ,  $c_A^0=2.6 \text{ g/l}$ ,  $D_A=10^{-9} \text{ m}^2/s$ ).



**Figure 12.** Total conversion time for  $\text{PbCO}_3$  at different initial HA concentrations ( $k_r=10^{-4}1/s$ ,  $D=0.02 \text{ m}$ ,  $D_A=10^{-9} \text{ m}^2/s$ ).



**Figure 13.** Total conversion time for three lead compounds ( $c_A = 2.6 \text{ g/l}$ ,  $k_r=10^{-4}1/s$ ,  $D=0.02 \text{ m}$ ,  $D_A=10^{-9} \text{ m}^2/s$ ).



**Figure 14.** Concentration profile at the center of the aggregate ( $c_A = 2.6 \text{ g/l}$ ,  $D_A=10^{-9} \text{ m}^2/s$ ,  $k_r=10^{-4}1/s$ ,  $c_B=100 \text{ mg/kg}$ ,  $D=0.02 \text{ m}$ , ).

$c_B$  concentration of lead compound in solid phase (mg/kg)  
 $c_P$  concentration of pyromorphite in the solid phase (mg/kg)  
 $c_A$  concentration of HA in the liquid phase ( $\text{kg/m}^3$ )

$\tau$  tortuosity of pores in the aggregate  
 $U$  velocity of flowing fluid (m/s)  
 $\nu$  viscosity of the fluid ( $\text{m}^2/\text{s}$ )