Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

MODELS FOR LEACHING OF POROUS MATERIALS

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Abstract

The release of soluble species contained in solidified/stabilized wastes are assessed by leaching tests. Interpretation of experimental results must be supported by precise modeling of the different phenomena involved hydrodynamics, dissolution, chemical interaction, diffusive transport.

The models are presented, which can apply according to the leaching scenario (with or without advection).

- solubilization shrinking core model,
- diffusionnal model,
- coupled dissolution/diffusion model.

1. Introduction

The Laboratory of Environmental Analysis of Industrial Systems and Processes (LAEPSI) of INSA, Lyon and the division POLDEN INSAVALOR have consecrated a significant part of their research over the past few years to the study of stabilized waste leaching tests. Interpretation of the results leads to the evaluation of the environmental quality of the obtained materials.

Solidification using hydraulic binders gives rise to porous monolithic materials. The pollutants initially contained in the wastes are confined and may even be stabilized within the solid matrix. Certain mechanisms of solidification/stabilization are well known, whereas others are still the object of research. There are numerous factors which govern waste solidification/stabilization. and their choice can be optimized in order to obtain materials with characteristics meeting the technical and environmental specifications of the considered scenarios : good mechanical strength, good leaching behaviour, etc...

The release of soluble species contained in a porous monolithic cement-based block in contact with water is the result of complex and coupled phenomena (at the block surface and within the block :

- water transfer in the porous medium up to saturation,
- dissolution of the species in the porewater according to the local chemical context,

- transport of species in solution due to the effect of concentration gradients,
- change of species solubility in the porewater (including possible reprecipitation) if the context of the latter has undergone certain modifications, due to the pH profile for example, following the release of pH controlling species (portlandite...).

The leaching studies of porous structures in different scenarios of liquid/solid contact lead to the use of several models to describe pollutant release.

Two cases can be distinguished :

1- Leaching of monoliths without advection : Several models can describe mass transfer in the porous solid: solubilization shrinking front model, diffusional model, coupled dissolution/transport model. ;

2- Leaching of granular beds with advection : in this case the hydrodynamics of the system must be taken into account by the percolation-leaching model. If the leaching imposes particular conditions of leachant flow around the solid, the mass transfer mechanisms (solubilization, diffusional transport etc...) must be integrated in the hydrodynamic model..

2. Leaching models without advection

2. 1. Solubilization shrinking core model

This model can describe the case of the main elements of the matrix without major chemical interactions (example : Ca, Na, K,...). It considers the coupling of the two phenomena : instantaneous *solubilization* (up to the saturation limit of the pore water solution) of the species present in the solid phase of the porous matrix saturated with water and its *diffusional transport* in the pore solution (characterized by the diffusion coefficient D), without chemical coupling with another species (the common ion effect is not taken into account).

The main constitutive hypotheses of the model are :

1- Initially, at t = 0, the solute has a uniform concentration in the solid equal to S0(kg/m3).

2- The solution is saturated by the solute with a constant concentration Csat, as long as the aqueous phase in the porous matrix is in equilibrium with the solid phase still containing the solute.

$$\begin{cases} 0 < x < X(t) & \dfrac{\partial C}{\partial t} = \dfrac{\partial^2 C}{\partial x^2} \\ x = X(t) & -D\left.\dfrac{\partial C}{\partial x}\right|_{x=X(t)} = S_0 \dfrac{\partial X}{\partial t} \\ x > X(t) & C = C_{sat},\quad S = S_0 \end{cases}$$

It is therefore a problem of a "shrinking front" : the mobility of the dissolution front is governed by the mass balance at the front position X(t).

The rate at which the dissolution front shrinks within the solid is proportional to the square root of time $X(t) = K\sqrt{t}$.

Between this front and the liquid interface, transport of pollutants in the pore water takes place by diffusion. On the other side of the front towards the core there is no mass transfer.
The parameters of the model are : C_{sat}, S_0 and D.

The concentration at the liquid/solid interface varies according to the leaching scenario. If renewal is sufficient, this concentration can be considered as zero.

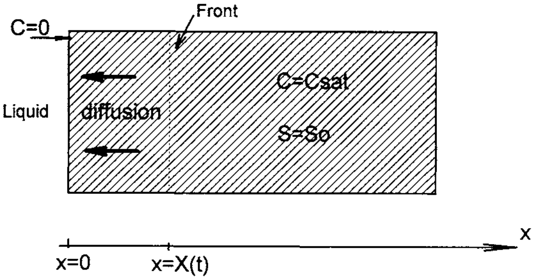

Fig. 1 : The shrinking front solubilization model (one species)

2. 2. Diffusional model

The diffusional model is widely used to interpret leaching tests (tank leaching test NEN 7345). Strictly speaking, this model describes the transport of one species initially present, completely dissolved in the pore water. This description can be extended to the case of very soluble elements whose solubility does not change according to the variable physico-chemical leaching context and which are instantaneously and quantitatively solubilized in the pore water : Na, K, Cl...)

Numerous experiments, in different scenarios, have shown that a diffusional model (based on Fick's law) can correctly describe the released flux J (kgs^{-1} m^{-2}) of the very soluble elements which are not constitutive elements of the solid matrix :

$$\vec{J}_n = - D_a \times \frac{\partial \vec{C}}{\partial n}$$

where D_a= apparent diffusion coefficient (m^2 s^{-1})
C = volumetric concentration, ($kg\ m^{-3}$)

Generally used assumptions for applying this equation are : isotropic porous media, in which the structure is constant with time. The solubilization is considered to be instantaneous and not mass limited. The concentration at the solid/liquid interface is zero (which is the case if water renewal is sufficient). The apparent diffusion coefficient D_a (in m^2/s) is assumed to remain constant in time and space, which implies, in particular, that the solid is saturated with water from the beginning of the process and that no physical or chemical alteration disturbs the diffusion phenomenon.

The fundamental diffusion equation becomes :

$$\frac{\partial C}{\partial t} = D_a \times \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right)$$

For a solid of infinite length ($x \in [0, \infty[$) in contact with the liquid via a normal plane surface of direction x, the flux of the leached material can be written :

$$J(t) = -D_a \left. \frac{\partial C}{\partial x} \right|_{x=0} = C_0 \times \frac{\sqrt{D_a}}{\sqrt{\pi t}}$$

if C_0 is the initial leachable concentration.

The two parameters C_0 and D_a can be identified by two distinct experimental tests (availability test and tank leaching test). We proposed an approach based on the simultaneous identification of the two diffusional model parameters, from only one tank leaching test if the leaching time is sufficient to reach depletion of the released species in the solid core of the leached sample. In figure 2 the values of the standard deviation z of the simulated and experimental sodium concentrations in the leachate are represented, according to the varying values of D_a and C_0. The optimal values of the parameters C_0 and D_a are used in figure 3 (continuous curve) to simulate the released sodium flux J ($mgs^{-1} m^{-2}$) in comparison with the average experimental flux (points).

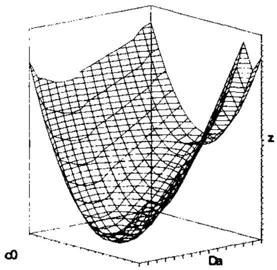

Fig. 2 : Optimal values of C_0 and D_a

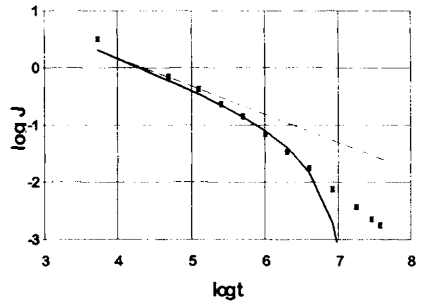

Fig. 3 : Simulation of Na release

Long term simulation for any scenario involving solid/leachate contact is then theoretically possible. The application limits of the model are reached when the physical characteristics of the material itself are modified (increased porosity, destruction of the porous structure...). We have also observed a 100 to 1000 times lower "residual flux" : the release continues although the defined (theoretical) diffusional flux has stopped. A possible explanation of this phenomenon could be the continuation of release of a less soluble phase after depletion of the more soluble phase.

For the same experiment, the comparison between the solution of the diffusional model (parameters : C_0 and D_a), and the shrinking core model (parameters C_{sat}, S_0 and D) shows that :

$$C_0 = A\sqrt{\frac{D}{D_a}} = \frac{KS_0}{2}\sqrt{\frac{\pi}{D_a}}\; e^{\left(\frac{K^2}{4D}\right)} \qquad \text{and} \qquad D_a = \left(\frac{C_{sat}}{C_0 \operatorname{erf}\frac{K}{2\sqrt{D}}}\right)^2 D$$

Based on the available experimental results (solute mass released in the leachate), it is not possible to distinguish between the two models : as long as the solid "remains" semi-infinite, the mass released is proportional to the square root of time. In conclusion, with respect to the initial hypothesis, the two models are equivalent for the modelling of the release of specific species. However, an important difference is that the concentration profile of the species in the pore water can be calculated from the shrinking core model.

2. 3. Coupled dissolution/diffusion model

This model must be considered in the case of elements whose solubility depends on the variation of the physico-chemical context, pH in particular (example : amphoteric metals).

Experiments have shown that amphoteric metals release is controlled by solubility in the pore water context. The pH evolution within the solid and especially at the solid/liquid interface is a significant parameter. Lead is a typical case of such behaviour. Pb additive release in a mortar elaborated from Portland cement (sequential leaching of identical samples of the same monolithic material containing PbO) in contact with different chemical contexts : demineralized water (W), controlled pH 5 and pH 10, alkaline water at pH 12.5 (AW) is presented in the figures below.

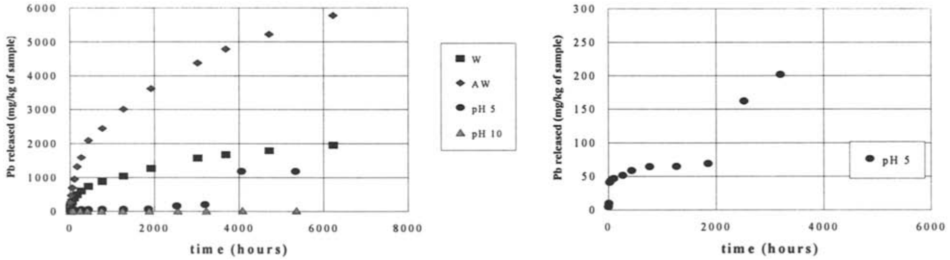

Fig. 4 : Leaching of Pb in different leachants

The release of Pb is sensitive to the chemical context of the leachant and cannot be described by the simple diffusional or shrinking core model.

A coupled dissolution/diffusion model can describe the release of chemically more complex species contained in a stable porous matrix in contact with water. In the case of a porous matrix containing two leachable components : calcium hydroxide and lead hydroxide, the modelling of release can be decomposed into several stages :

- release of portlandite, described by a shrinking front model ;

- calculation of the induced pH profile, assuming that local chemical equilibrium takes place in the porewater ;
- determination of local lead solubility (by calculation or from specific experimental determination) ;
- description and calculation of lead transport by diffusion in the porewater and/or at the solid/liquid interface.

Different simulations were carried out and compared to the results obtained from leaching of cement-based matrixes containing lead. The coupled dissolution/diffusion model allows representation of the leaching tests results using demineralized water and confirms the interfacial character of lead release. As long as lead in solid form is present in the matrix zone near the leaching surface of the matrix, its release is controlled by a solubilization phenomenon at the solid/liquid interface. In this case, the leaching model can be simplified : diffusional transport of lead within the matrix can be neglected.

A model based on the shrinking core model to describe the calcium release from which the pH evolution at the solid/liquid interface is assessed (Figure 5) and variable lead solubility according to this pH (assessed in an Acid Neutralization Procedure) allows a good representation of the phenomena (Figure 6). The case of lead is specific : the release seems to be governed (on the time scale of our laboratory leaching tests) by a lead solubilization phenomenon at the solid/liquid interface, itself governed by the pH as the relevant parameter.

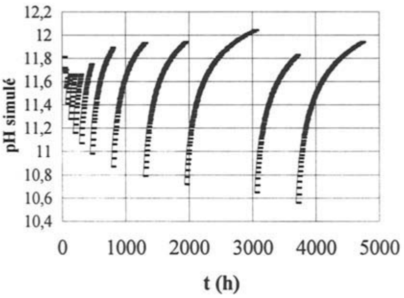

Figure 5 : Simulation of pH evolution near the solid/liquid interface.

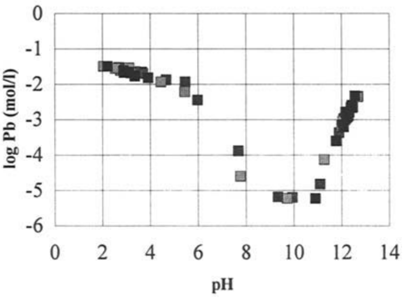

Figure 6 : Experimental solubility curve according to pH

The observed discontinuities on the simulation of pH evolution at the matrix cement/solution interface result from the sequential character of the leaching test carried out (periodical renewal of the leachant).

Knowledge of the pH near the matrix cement/solution interface allows, **from the experimental solubility curve**, evaluation of the **lead concentration at saturation** in this zone. The quantity of lead released can be estimated via an **interfacial transfer coefficient** (figure 7).

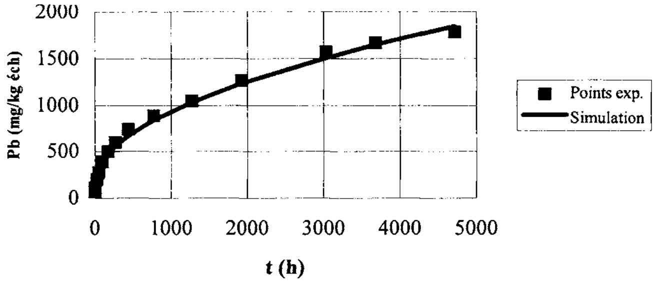

Figure 7 : Simulation of lead release. Leaching with demineralized water

3. Leaching models with advection

Leaching of granulate materials is usually carried out by percolation tests. Transport by advection must then be taken into account.

The first level of modelling concerns characterization of the hydrodynamic regime of liquid through the column. Dispersion must be taken into account.

The general equation governing solute transport in the mobile liquid phase is as follows (one dimensional model) :

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) - v\frac{\partial C}{\partial x} + R$$

where v is the velocity of the liquid, D the hydraulic dispersion coefficient and R a source term (corresponding to dissolution flux). The phenomenon of advection-dispersion can classically be translated by a model consisting of n identical contactors of continuous stirred open reactor type each containing a mobile phase in contact with the solid phase. The presence of stagnant zones can also be taken into account. The porous solid is therefore in contact, in each reactor, with the mobile liquid as well as the stagnant liquid. The solute is exchanged between the solid phase and the liquid phase as well as between the mobile and immobile liquid phases. In the following figure, the hydrodynamic model of percolation-leaching is presented.

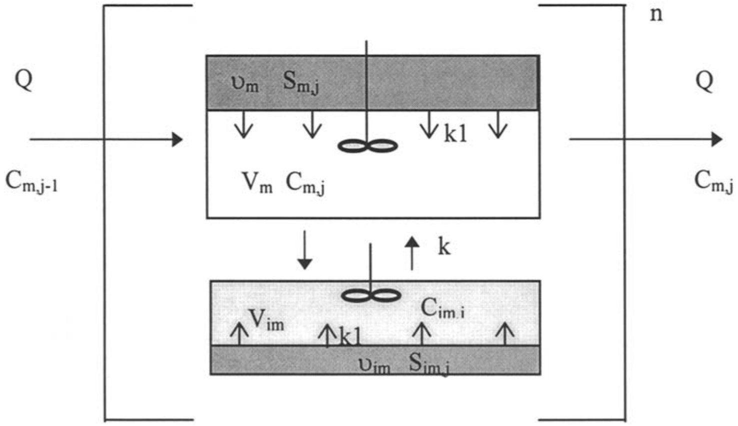

Figure 8 : Hydrodynamic model of percolation-leaching of porous granular material

The experimental use of a tracer allows identification of model parameters (n number of reactors, mobile fraction f_m of the volume and transfer coefficient K (between the two liquid zones). But problems of interaction between the porous medium and the tracer (diffusive transport in the porous system, surface sorption phenomena, etc...) may complicate interpretation of experimental results.

The balance of tracer in the cell j for time i*Δt, while flowing and in the stagnant zone (Coats and Smith model), is :

$$QC^i_{m,j-1} - QC^i_{m,j} = \frac{d}{dt}\left(\frac{V}{n}C^i_j\right) = f_m \frac{V}{n}\frac{dC^i_{m,j}}{dt} + f_{im}\frac{V}{n}\frac{dC^i_{im,j}}{dt}$$

$$\frac{dC^i_{im,j}}{dt} = K(C^i_{m,j} - C^i_{im,j})$$

where :

$C_{m,j}$: the volumetric concentration of tracer in the mobile fraction and in the cell j, kg/m^3,
$C_{im,j}$: the volumetric concentration of tracer in the stagnant zone and in the cell j, kg/m^3,
V : the volume accessible to the fluid, m^3,
f_m : the mobile fraction in the liquid phase,
f_{im} : the immobile fraction in the liquid phase,
K : the mass transfer coefficient, h^{-1}.

In the following graph the experimental and simulated results are presented for the behaviour of the lithium ion used as hydrodynamic tracer during the leaching of slags. The model takes into account physico-chemical interferences between the tracer and slags : the hypothesis used neglects diffusive transport in the porous system, only taking into account sorption phenomena. The parameters used for the simulation are : n=15, f_m =0.8 and K=4h^{-1}.

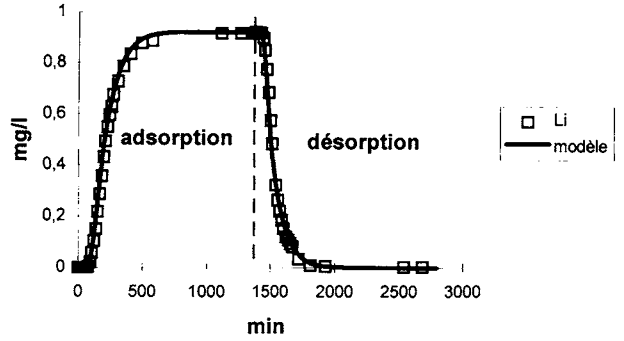

Fig. 9 : Identification of hydraulic regime using a tracer in a column containing leached slags

The model of leaching with advection must take into account the release of the solute by transfer from the porous solid matrix to the flowing liquid (source term). The models describing the solute transfer in the porous material are either the dissolution shrinking front or purely diffusional. The corresponding models have been presented above. The global model is therefore applicable to elements whose solubility does not vary according to modifications in the local physico-chemical context in the column.

The results for calcium release contained in the slags in a percolation column are presented :

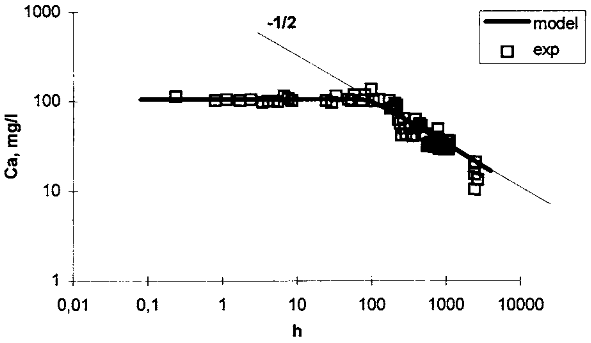

Figure 10 : Calcium release from slags by percolation leaching

Three periods can be demonstrated :

- during about one hundred hours, the leachate contains a practically constant concentration and equal to the initial concentration corresponding to the equilibrium of the aqueous solution in prolonged contact with the slags ;
- in a second period, calcium concentration decreases in the leachate according to a law inversely proportional to the square root of time : calcium release is controlled by diffusional transport in the granular solid ;
- after 3000 hours, calcium concentration falls, which corresponds to depletion in the porous solid.

4. Conclusion

The different models presented here can be used to describe the release of soluble species contained in the porous monolithic or granular materials during leaching. The hydrodynamic scenario must be considered to determine the limiting stage of the mass transfer process, taking into account possible evolution of the solubility of the released species.

The development of leaching tests aiming to characterize pollutant retention in solidified wastes must be carried out with great care and supported by precise modelling of the different phenomena involved.

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