

Leaching behavior of pollutants in stabilized/solidified wastes

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Abstract

The objective of the study is to characterize pollutant retention in wastes solidified with hydraulic binders in order to predict the long term leaching behavior. The stabilized/solidified wastes are APC MSW (air pollution control residues from municipal solid waste incineration), lead secondary smelting slag and different salts. The binders used are ordinary Portland cement (OPC 55) or blast furnace slag cement (CLK 45) and additives, such as metakaolin. Leaching tests are used in the characterization procedure. Modelling of the observed leaching behavior is conducted to improve the description of the physical and chemical phenomena involved in the release of soluble species. The main results of the study allow a distinction to be made between the species whose solubility is not sensitive to the chemical context of the porewater, and the other species, such as amphoteric metals, whose solubility is sensitive to the context (especially the pH). In the first case, a diffusion or shrinking front model is appropriate. In the second case, a coupled solubilization/diffusion model must be developed in order to describe the leaching behavior of heavy metals (lead, etc.) contained in the stabilized/solidified wastes. © 1997 Elsevier Science B.V.

Keywords: Leaching; Stabilization/solidification

1. Introduction

In France, industrialization of stabilization/solidification processes using hydraulic binders must be developed in short term to meet the new regulatory standards for

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landfill admission. The technical and economical aspects of these processes are very important, in particular, to ensure retention of soluble species in the solidified material.

The materials obtained are of porous nature and retention of soluble pollutants must be characterized using specific tests. Leaching tests are appropriate for this aim. Physico-chemical phenomena leading to dissolution of pollutants in the porewater of the porous matrix and to their transport towards the leaching solution are complex, and interpretation of the experimental results must be carried out with caution to guarantee sufficient reliability and to allow extrapolation of laboratory tests to an industrial scale and thereby judge the quality of the product.

The identification and modelling of the leaching mechanisms may also contribute towards a better understanding of the very complex physico-chemical phenomena involved in pollutant release.

2. Experimental

To characterize the release of soluble species contained in a waste solidified with an hydraulic binder, several industrial wastes, solidified in different physico-chemical contexts were studied, in particular [1] APC MSW (air pollution control residues from municipal solid waste incineration) and lead secondary smelting slag.

Two types of cement (ordinary Portland cement, OPC, and blast furnace slag cement, CLK) and a pouzzolanic binder (metakaolin) were used. The mortars were made to the following recipe: 0.3 parts binder, 1 part sand, 0.7 parts waste. A sand with granulometry of 90% between 1.6 and 3.15 mm was used. The quantity of demineralized water was established according to the waste behavior. NaOH was added to control the pH of the cement paste. The composition of the solidified materials is shown in Table 1.

The mixing and compacting of the mortar were carried out according to points 6.3 and 7.2 of the standard procedure NF EN 196-1 [2].

The specimens ($4 \times 4 \times 8 \text{ cm}^3$) were made by dry cutting of the blocks, 28 days after their preparation.

Table 1
Composition of the solidified materials I to IV (kg)

Mortar	OPC	CLK	Pouzzolanic binder	NaOH	Sand	Slag	APC MSW	Water
I g	5.81	–	–	–	19.36	–	13.55	9.68
II g	–	5.81	–	–	19.36	–	13.55	9.68
III r	3.11	–	–	0.06	10.56	–	7.39	5.28
IV r	1.9	–	1.27	–	10.56	–	7.39	5.28
I s	5.81	–	–	–	19.36	13.55	–	4.4
II s	–	5.81	–	–	19.36	13.55	–	4.4
III s	3.11	–	–	0.06	10.56	7.392	–	2.3
IV s	1.9	–	1.27	–	10.56	7.392	–	2.58

Table 2
Content of elements of the leached blocks

Block	Na (mg)	Cl (mg)	Pb (mg)
I r	1397	12568	179
II r	1463	12332	174
III r	1630	11625	166
IV r	1302	11775	169
I s	9772	1484	9977
II s	11039	1818	11129
III s	10484	1526	10264
IV s	10331	1595	10555

2.1. Conventional tests and diffusional interpretation

We have developed a leaching test based on the NVN 7345 tank leaching test for solid products [3].

The leaching tests were conducted on blocks of $4 \times 4 \times 8$ cm³, contacted with demineralized water ($25 \pm 3^\circ\text{C}$) at a liquid/solid ratio = 10.

The solid–solution contact times were 6, 18, 24, 48, 96, 192, 384, 768, 1704, 3600, 2256 and 2976 h for each series.

The leachates were analyzed after filtration (0.45 μm): Na, Pb by atomic absorption, Cl by ion chromatography and the parameters (pH, potential, conductivity) were determined (Table 2). The results have been reported in [1].

A first experimental series was obtained by leaching with demineralized water, without controlling pH. The analyzed leachates concentrations are very low (Pb < 0.2 mg l⁻¹ in the 'r' leachates and < 4 mg l⁻¹ in the 's' leachates; Na < 0.1 g l⁻¹ in the 'r' leachates and < 0.4 g l⁻¹ in the 's' leachates; Cl < 0.7 g l⁻¹ in the 'r' leachates and < 50 mg l⁻¹ in the 's' leachates). Table 3 shows the percentages of the released fraction over 503 days as compared to the initial mass of each element present in the block (Table 2).

Table 3
Percentage release after 503 days (compared to the total initial mass present in the block)

% Release	Na	Cl	Pb
I r	97	90	2
II r	100	85	0.6
III r	100	88	2
IV r	92	91	1
I s	84	61	0.4
II s	91	68	0.1
III s	80	56	0.5
IV s	85	56	0.1

From the results, two types of leaching behavior could be distinguished:

- (1) Easily soluble elements are practically totally released within the period of time analyzed. This release is only slightly dependant on the solidification recipe (e.g., Na).
- (2) Less (or only slightly) soluble elements are only slightly released (e.g., Pb).

The different mechanisms proposed for the transfer of soluble species during leaching of a solid block are: (1) Washing of the surface at the beginning of the contact (solid/solution), (2) Solubilization of the matrix containing the pollutants, and (3) Release of the soluble species within the porous matrix, governed by a diffusional mechanism [4].

In our case the diffusional mechanism is supposed to control the long term release of the soluble elements contained in the very insoluble cement matrix.

The normal flux of material is therefore controlled by diffusion in the porous matrix and obeys Fick's law [5]:

$$\vec{J}_0 = -D_a \frac{\partial \vec{C}}{\partial n} \quad (1)$$

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

Eq. (1) applies to isotropic media, in which the structure and diffusive properties remain constant with time. This assumption is generally used [4–10].

Eq. (1), in the case where the apparent diffusion coefficient D_a is constant, allows us to obtain the fundamental differential equation of diffusion in an isotropic medium.

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

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 [10]:

$$J(t) = -D_a \frac{\partial C}{\partial x} \Big|_{x=0} = C_0 \times \frac{\sqrt{D_a}}{\sqrt{\pi t}} \quad (3)$$

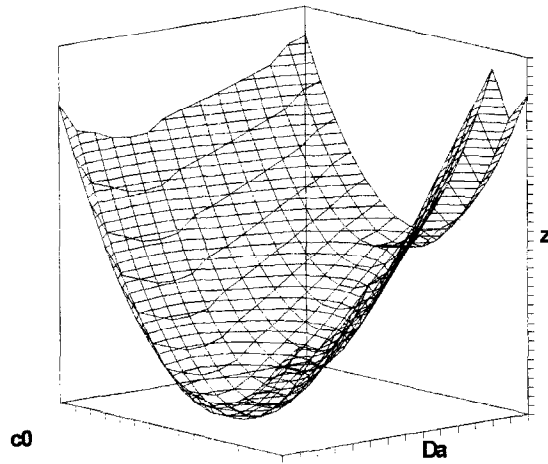
if C_0 is the initial leachable concentration and if the concentration at the solid/liquid interface, $C_{\text{interface}}$, is zero (which is the case if water renewal is sufficient). This assumption is generally used in the classical leaching test interpretation [4,7,18].

The apparent diffusion coefficient D_a (in $\text{m}^2 \text{s}^{-1}$) 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.

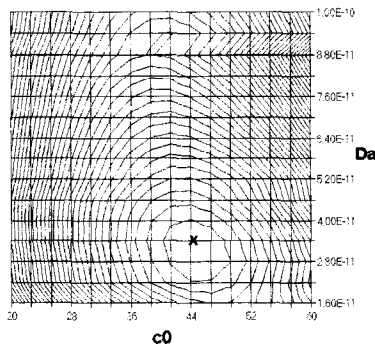
The experimental identification of the product $C_0 \sqrt{D_a}$ allows determination of the diffusion coefficient if C_0 has been determined by a preliminary experiment [4,8].

We proposed a new approach based on the simultaneous identification of the two diffusional model parameters, C_0 and D_a , from only one tank leaching test [1,5].

For the case of a solid of finite dimensions, it is possible to identify simultaneously the parameters C_0 and D_a of the model if the leaching time is sufficient to reach depletion of the released species in the solid core [1].



1.a



1.b

Fig. 1. Optimal determination of C_0 and D_a model parameters.

Solutions of the equation for diffusion (Eq. (2)) in the case of a finite volume can in fact be calculated by numerical techniques [8,10,11].

We have tried to confirm the ‘diffusional’ behavior of the different elements by comparing experimental results to those obtained by simulation. The values of the parameters, C_0 and D_a , corresponding to the simulation have been identified using Rosenbrock’s method [12]. In Fig. 1a, the values of the standard deviation z :

$$z = \sum_{i=1}^n (C_{\text{exp}} - C_{\text{sim}})^2 \tag{4}$$

are represented in order, according to the varying values of D_a and C_0 .

Table 4
Identification of the parameters of the diffusional model

Block	Na			Cl		
	C_0 (kg m ⁻³)	C_0/C (%)	D_a ($\times 10^{-11}$ m ² s ⁻¹)	C_0 (kg m ⁻³)	C_0/C %	D_a ($\times 10^{-11}$ m ² s ⁻¹)
I r	9.8	90	18.4	86.9	89	11.8
II r	9.7	85	20.3	73.8	77	11.4
III r	12.9	101	22.9	76.2	84	14.1
IV r	8.9	88	18.9	74	80	7.3
I s	45.6	60	3.3	4.7	41	4
II s	54.2	63	3.1	7.3	51	2.7
III s	46.5	57	4.6	5.1	43	6.6
IV s	60.6	75	4.5	6.9	55	11.4

The example illustrates the case of sodium leaching (sample I s). A minimum value exists for: $C_0 = 45.6$ kg m⁻³ and $D_a = 3.3 \times 10^{-11}$ m² s⁻¹. Projection of the isocriteria curves in the plane C_0 - D_a shows this minimum, situated between $D_a = 2.2 \times 10^{-11}$ and $D_a = 4.10^{-11}$ m² s⁻¹, and respectively between 41 and 49 kg m⁻³ for C_0 (Fig. 1b).

A parameter sensitivity study of the method applied gives an accuracy to the order of 10% for the estimation of C_0 , the available release potential [1].

Table 4 shows the calculated values of C_0 compared to the total concentration C present in the sample, C_0/C (%).

It can be observed that the values of the total content fit with the values of the available potential release C_0 , identified by the method presented here.

2.2. Experimental results and determination of parameters C_0 and D_a

The logarithm data representations (logarithm of release flux J [kg m⁻² s⁻¹] versus the logarithm of time [s]) are very sensitive for judging the quality of the description of phenomena by the diffusional model.

In Figs. 2–5, the results obtained for some of the studied cases are shown: the straight dashed line with the slope -0.5 represents the diffusional release flux for the

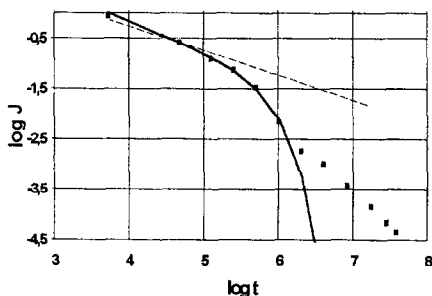


Fig. 2. Leaching of Na: I r block.

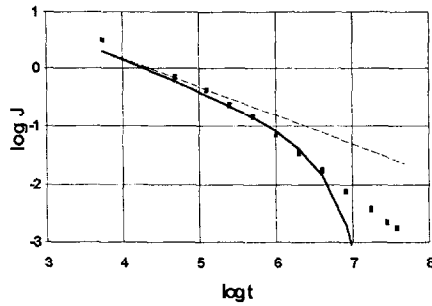


Fig. 3. Leaching of Na: I s block.

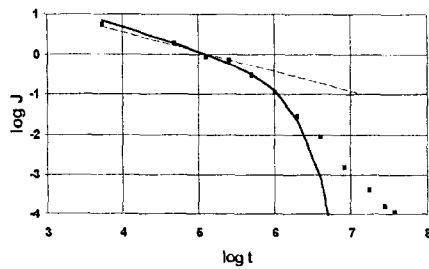


Fig. 4. Leaching of Cl: I r block.

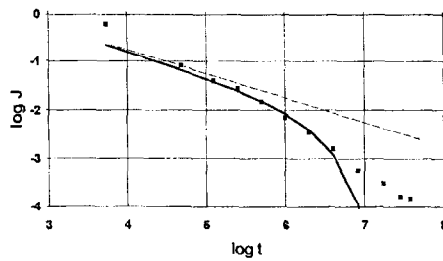


Fig. 5. Leaching of Cl: I s block.

infinite length solid, the continuous curve represents our simulation results and the points represent the average experimental flux J_i .

At the beginning of the process, and excluding the first point, where the part of the flux J due to an initial washing phenomenon may have an influence, the hypotheses of the semi-infinite medium remains valid (Eq. (3)). The graph $\log J/\log t$ is therefore a straight line with a slope of $-1/2$. The continuous curve represents the mathematical simulation of diffusional release after identification of parameters C_0 and D_a .

The estimation of the elemental momentaneous flux through the specimens surface is obtained from the released mass during a leaching interval. For each leaching period $[t_i,$

t_{i+1}] the average experimental flux J_i is graphically represented by a point at the time T_i , where [1,6]:

$$\sqrt{T_i} = \frac{1}{2}(\sqrt{t_{i+1}} + \sqrt{t_i})$$

It appears clearly in all cases that depletion of the solid core is noticeable after about thirty hours: the semi-infinite medium assumption is not still valid.

In conclusion, it is possible to determine C_0 and D_a simultaneously where the results of the washing test carried out on the monolithic sample show a clearly diffusional behavior with measurable depletion (Table 4).

The results obtained for the apparent diffusion coefficient fall within the range of values published for these elements in the literature [1].

A certain 'residual' flux for contact times of more than 3000 h should be noted. We will come back to this later.

3. Limits of the diffusional model and chemical sensitivity

The results of conventional leaching tests with demineralized water show that the behavior of certain elements depends on their chemical 'complexity'. In the case of calcium, for example, a possible influence can be noted due to carbonation of the blocks [1,6]. The chemical influence of the leaching solution (in particular the pH) on the leaching behavior of pollutants is obvious, as in the case of lead.

We have developed 4 types of leaching test: using a solution saturated with calcium hydroxide, (pH ca. 12.4), and in a controlled atmosphere in leaching tanks containing either: air, nitrogen or carbon dioxide [1].

3.1. Case of sodium

The results show the sensitivity of release to experimental chemical conditions. This sensitivity may be due to a specific action of the leaching solution on the matrix (dissolution, carbonation etc). The APC MSW blocks have a lower concentration C_0 of sodium than the slag blocks, which explains their relatively greater sensitivity to chemical conditions during leaching.

The blocks I r leached under nitrogen or carbon dioxide are an example: the semi-infinite model for release does not seem applicable for the beginning of leaching under nitrogen (Fig. 6) whereas it can be applied in the second case (Fig. 7).

The upper straight dashed line with the slope -0.5 represents the initial semi infinite diffusional release flux. The lower straight dashed line with the same slope represents the residual diffusional release flux. The points represent the average experimental flux.

It can be noted that a variation in kinetics according to the inverse square root of time (Eq. (3)) well describes the residual flux (Figs. 6 and 7). This observation is confirmed in the case of leaching of sodium in APC MSW blocks (type I and IV, Figs. 8–11) and is independent of leaching conditions.

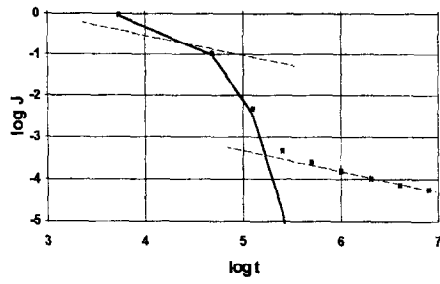


Fig. 6. Leaching of Na: I r block, N₂.

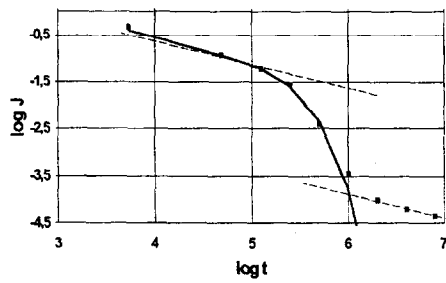


Fig. 7. Leaching of Na: I r block, CO₂.

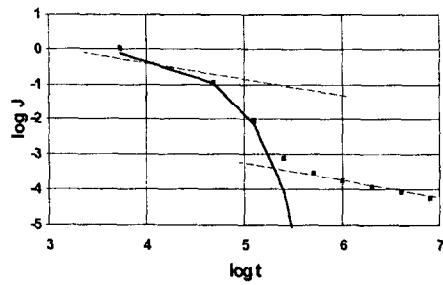


Fig. 8. Leaching of Na: I r block, Ca(OH)₂.

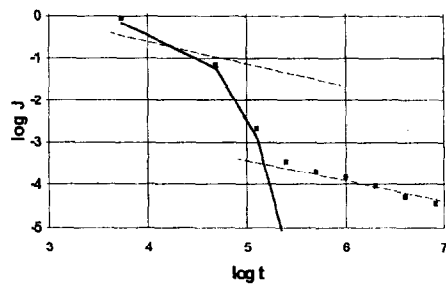


Fig. 9. Leaching of Na: I r block, air.

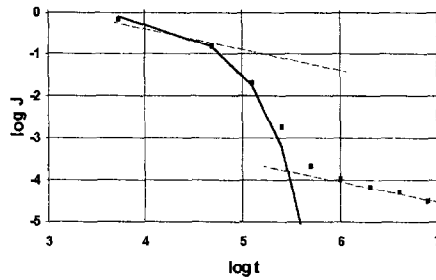


Fig. 10. Leaching of Na: IV r block.

We can therefore suppose that two ‘forms’ of sodium are leached:

(1) More readily available for leaching, whose concentration is identified C_0 . It is released according to the diffusional law (diffusion coefficient D_a). Both parameters can be estimated by applying the diffusional model. The simulated diffusional release flux J in the case of the finite solid model is graphically represented by a continuous curve.

(2) Another, less available form, which causes the ‘residual’ flux (this flux is graphically represented by the lower straight dashed line with the slope -0.5). Quantitatively speaking, the residual flux is low (about 1000 times lower than the original flux in the APC MSW series). Dissolution of a constitutive phase of the matrix itself containing sodium may be at the origin of this phenomenon [6].

Another hypothesis could be the formation of a layer of silica gel on the surface, thus constituting a resistance to the transport of matter [13]. However, such a phenomenon should be the same for all the species released, which has not been observed experimentally for chlorine or calcium to the same extent [1,6].

The appearance of ‘residual’ flux means that other physico-chemical phenomena are involved in the release of new quantities of solutes and/or in the modification of the physical and chemical characteristics of the matrix.

It must be noted that, for sodium or chlorine, variations in leaching behavior are slight as compared to the chemical characteristics of the leaching solutions.

Our approach confirms the diffusional depletion leaching mechanism for sodium and chlorine. After 60–80 days (10^6 s) of leaching (about 90% of Na or Cl are leached) a ‘residual’ flux appears; this flux is greater than the theoretical diffusional flux.

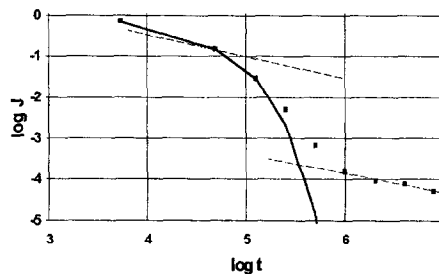


Fig. 11. Leaching of Na: IV r block, Ca(OH)_2 .

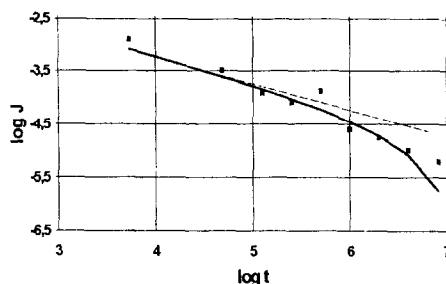


Fig. 12. Leaching of Pb: I r block.

3.2. Case of lead

Release of lead during tests using demineralized water is low: a quantity varying between 0.06% (II s, IV s) and 2.22% (III r) of the total content is released after 503 days.

One of the first question is: may a simple diffusional description fit the lead leaching behavior well?

In Figs. 12 and 13, a diffusional simulation of Pb release has been proposed. The straight lines of slope $-1/2$ (semi-infinite diffusional model) are drawn. The optimal values identified for the parameters of the model are, for I r: $C_0 = 0.02 \text{ kg m}^{-3}$, $D_a = 2.5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and for III r: $C_0 = 0.03 \text{ kg m}^{-3}$, $D_a = 1.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

Lead is released from the beginning of the test, at a level which varies according to the binder used and therefore according to the pH level in the porewater: III > I > IV > II.

For the tests conducted on slag, the diffusional release model cannot be applied to the lead experimental data (Figs. 14 and 15; the straight lines of slope $-1/2$ are drawn).

The lead leaching behavior in various leaching solutions brings us to give up its simple diffusional modelling (see below).

The influence of the different leaching solutions on lead release is presented in Table 5.

It can be observed that solutions saturated with calcium hydroxide and carbon dioxide have a greater influence on release (4 times for block I s, 14 times for block IV s and 41 times for block IV r). Air and CO_2 are almost the same.

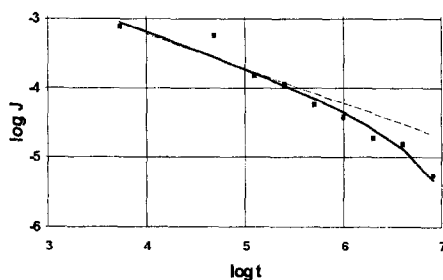


Fig. 13. Leaching of Pb: III r block.

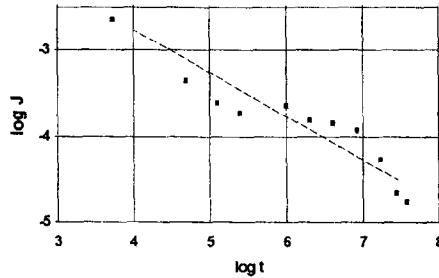


Fig. 14. Leaching of Pb: I s block.

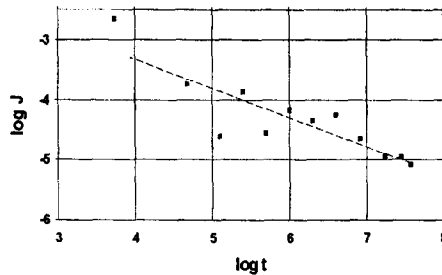


Fig. 15. Leaching of Pb: II s block.

In Figs. 16–19, we have grouped, according to block (same composition and same dimensions), the values of lead flux (logarithm of release flux J [$\text{kg m}^{-2} \text{s}^{-1}$] against the logarithm of time [s]).

The following observations can be made:

(1) The initial lead content (concentration and/or speciation) in the solidified material influences the level of release: solidified APC MSW release a flux of Pb, on average, 10 to 100 times lower than solidified slag.

(2) The type of binder used (OPC + pouzzolanic binders for the recipe IV, OPC for recipe I) has no significant influence on Pb release.

Table 5

Variation of lead release as compared to release in demineralized water using different leaching solutions (%)

Block	Solutions saturated with			
	CO ₂	Air	Ca(OH) ₂	N ₂
I r	-84	-85	47	-7
I s	-97	-95	390	-39
IV r	106	-57.0	4100	4
IV s	-25	-100	1400	-29

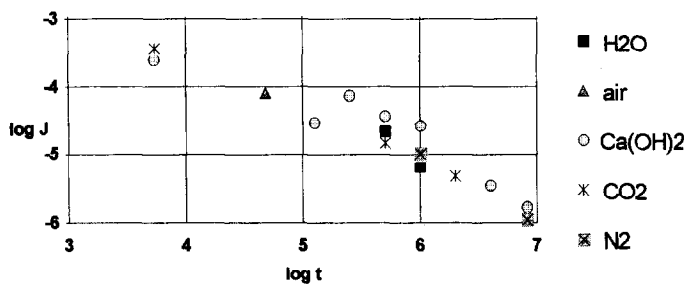


Fig. 16. Leaching of lead: I r blocks.

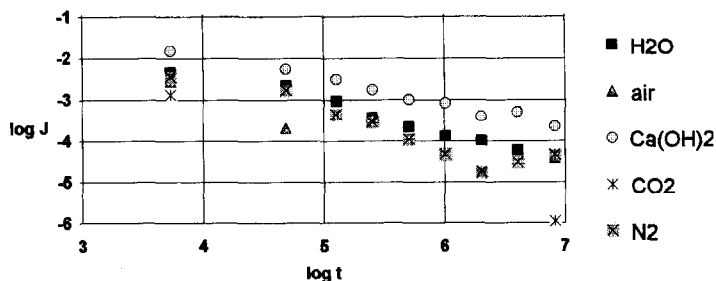


Fig. 17. Leaching of lead: I s blocks.

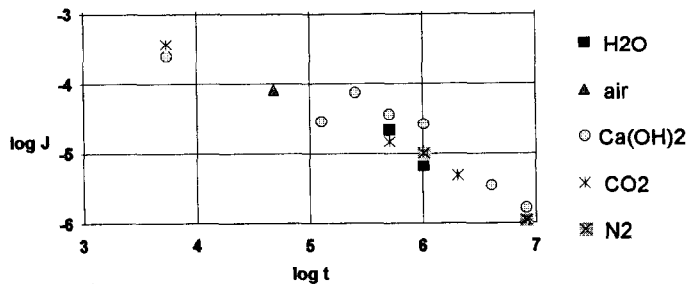


Fig. 18. Leaching of lead: IV r blocks.

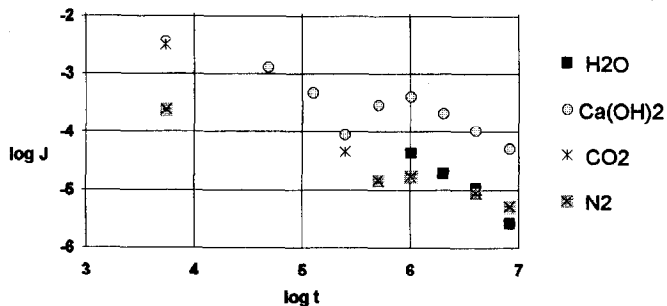


Fig. 19. Leaching of lead: IV s blocks.

(3) The influence of the different leaching solutions on flux gives two extreme cases:

(a) The solution saturated with lime gives the greatest flux of Pb. It can be assumed that it's due to the pH influence on Pb solubility (pH between 12 and 13).

(b) The solution saturated with carbon dioxide (pH between 6 and 7) gives rise to the lowest flux of Pb.

The release of Pb when the solution is in contact with air is comparable to that observed when a solution saturated with carbon dioxide is used. This is probably due to absorption of atmospheric CO₂ in the leaching solution, rich in lime leached by the solidified materials. However, the pH values of the two types of leaching differ: neutral or slightly acidic for leaching under carbon dioxide (6 to 7), basic (10 to 12) in the other case.

The parameter which seems to influence Pb (amphoteric metal) release the most is the pH of the leaching solution. This parameter is influenced by the composition of the leaching solution: although leaching in presence of carbon dioxide generates a pH slightly lower than 7, the proportion of lead released in these cases is lower than that obtained using other leaching solutions.

The action of carbon dioxide seems to influence the retention of Pb by the matrix more than for the other elements analyzed [1]. This can imply a D_a changing, for example following a matrix carbonation.

(4) The release of other elements can be influenced by evolution of the matrix itself, especially if so called 'corrosive' leaching solutions are used (for example, solutions containing carbon dioxide) [1,6].

(5) Flux discontinuity is sometimes observed. The diffusional model is not appropriate to describe the release of lead, an amphoteric metal with a complex chemical behavior.

In conclusion, the leaching behavior of lead must be interpreted by taking into account the chemistry of the phenomena involved and especially the solubility of lead in the porewater during leaching.

4. Models for release coupling solubilization/diffusion

The experimental results have shown that the diffusional model is not valid for leaching of amphoteric metals (e.g., Pb) whose solubility depends on the chemical context [14].

The pH of the porewater of a cement matrix is close to that of a solution saturated with calcium hydroxide (ca. 12.4), the main product of hydration reactions. When lime is released, the pH within the solidified material varies due to the modification of the solubility of amphoteric metals. Leaching of metallic species therefore depends on pH and the composition of the porewater which varies with the leaching of the different chemical species present.

The models below aim to describe a coupling of the two phenomena: solubilization of the species present in the solid phase of the porous matrix saturated with water and diffusional transport.

4.1. Shrinking front model

4.1.1. Case of a single soluble species without chemical interactions. Analytical resolution

This model describes the release of lime, without coupling with another species. A similar model was developed for the case of the acid leaching of cement S/S wastes [9]. The constitutive hypotheses of the model are [15]:

(1) Initially, $t = 0$, the solute has a uniform concentration equal to S_0 (kg m^{-3}).

(2) The solution is saturated by the solute with a concentration C_{sat} . As long as the aqueous phase in the porous matrix is in equilibrium with the solid phase still containing the solute, the concentration is equal to the saturation concentration C_{sat} .

Solubilization is assumed to be instantaneous.

The effect of the presence of a common ion in the solution is not taken into account.

(3) The transfer of matter in the porous matrix takes place by diffusion, characterized by the diffusion coefficient D .

(4) The transfer of matter at the solid–liquid interface takes place without resistance, the concentration of the solute at the solid–liquid interface is zero.

$$\begin{cases} 0 < x < X(t) & \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} \\ x = X(t) & -D \frac{\partial C}{\partial x} \Big|_{x=X(t)} = S_0 \frac{\partial X}{\partial t} \\ x > X(t) & C = C_{\text{sat}}, S = S_0 \end{cases} \quad (5)$$

It is therefore a problem of a ‘shrinking front’: the mobility of the dissolution front is governed by the mass balance at $x = X(t)$. Between this front and liquid interface, transport of pollutants takes place by diffusion. On the other side of the front towards the core there is no mass transfer (Fig. 20).

The parameters of the model are C_{sat} , S_0 and D .

The analytical solution to this kind of problem exists, in particular for the case of thermal transfer with change of state [16].

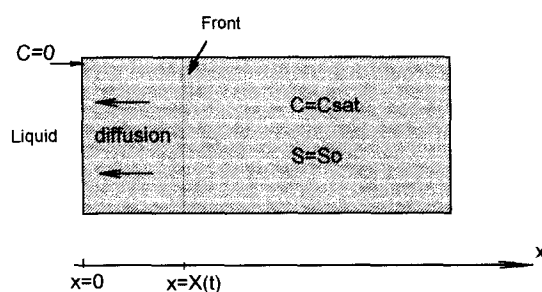


Fig. 20. Diagram of the shrinking front model (one species).

The rate at which the dissolution front shrinks within the solid, identified by its position $X(t)$, is proportional to the square root of time:

$$X(t) = K\sqrt{t} \quad (6)$$

The analytical solution of the diffusion equation, in the conditions of application of the model is:

$$C(x,t) = A \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad \text{where } A \text{ is a constant} \quad (7)$$

For $x = X$ (at the front):

$$\frac{S_0 K}{2D\sqrt{t}} = \frac{A}{\sqrt{\pi Dt}} e^{-\frac{K^2}{4D}} \quad (8)$$

The solution is expressed according to two constants, A and K , which verify the two following equations:

$$C_{\text{sat}} = \frac{\sqrt{\pi} S_0 K}{2\sqrt{D}} e^{(\frac{K}{2\sqrt{D}})^2} \operatorname{erf} \left(\frac{K}{2\sqrt{D}} \right) \quad (9)$$

$$A = \frac{\sqrt{\pi} S_0 K}{2\sqrt{D}} e^{(\frac{K}{2\sqrt{D}})^2} \quad (10)$$

The flux of solute released at the liquid/solid interface is therefore:

$$J(t) = -D \frac{\partial C}{\partial x} \Big|_{x=0} = A \times \frac{\sqrt{D}}{\sqrt{\pi t}} \quad (11)$$

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

$$C_0 = A \sqrt{\frac{D}{D_a}} = \frac{KS_0}{2} \sqrt{\frac{\pi}{D_a}} e^{(\frac{K^2}{4D})} \quad (12)$$

and:

$$D_a = \left(\frac{C_{\text{sat}}}{C_0 \operatorname{erf} \frac{K}{2\sqrt{D}}} \right)^2 D \quad (13)$$

From the point of view of the available experimental results (solute mass released in the leachate), it is not possible to distinguish between the model introduced here and the diffusional model presented before: as long as the solid 'remains' semi-infinite, the mass released is proportional to the square root of time.

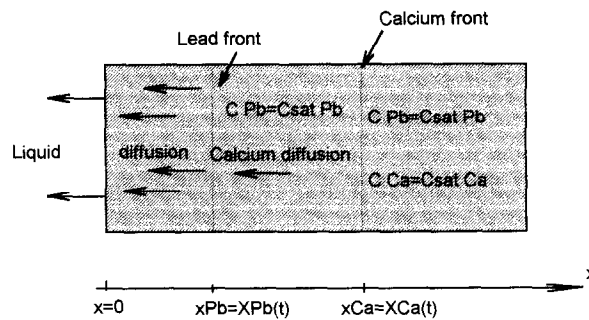


Fig. 21. Diagram of the shrinking front model (two species).

4.1.2. Case of two soluble species with chemical interactions. Mathematical resolution

In this case, the following facts must be taken into account:

- (1) The soluble species interact in the liquid phase, interactions which become more noticeable, in particular when high concentrations are present (as in the porewater),
- (2) The leached samples are of finite dimensions

The concentration at the interface is not constantly zero.

A numerical approach therefore becomes necessary. As an illustration, we apply it to an experimental case observed: the release of Pb by the mortars leached, which contain calcium hydroxide. In Fig. 21, we imagine the case of leaching on only one side of the sample.

We suppose that three regions can be identified:

(1) The zone within the solid near the liquid–solid interface, in which the solid forms of lead and calcium have been dissolved. The quantities of Ca and Pb in the porewater of this zone are transported, by diffusion, towards the liquid interface.

(2) The second zone, nearer the solid core, in which solid $\text{Ca}(\text{OH})_2$ has been depleted. Lead hydroxide in the solid form is still present and the porewater is therefore saturated with lead. In this region, the calcium is transported by diffusion. The concentrations of lead may vary in solution and/or in the solid phase, according to the varying solubility of lead due to modifications in the pH of the porewater.

(3) The third zone, in which two solid phases are present: there is no transfer of matter.

4.2. Coupled model: dissolution / diffusion

The model presented below is a generalization of the ones above. It has been developed in collaboration with the Laboratory of mathematical modelling and scientific calculations at INSA of Lyon. This model, which couples dissolution and diffusional transport, allows us to describe the release of ions contained in a stable composite porous matrix in contact with water [16,17]. It aims to describe, in a general way, transfer of soluble chemical species in a porous matrix.

4.2.1. Mathematical formulation

The model considers the phenomena on a macroscopic scale, it supposes that the activity in solution can be approximated to the concentration and that transport only takes place by diffusion (due to the low permeability of the matrix, convection is considered as negligible).

The main hypotheses are: the reactions in the liquid phase are in equilibrium, the porosity θ of the matrix is constant, the monodimensional diffusive transport is described for each species by a constant diffusion coefficient D_k .

The equation which translates the principle of mass conservation can be written:

$$\theta \frac{\partial C_k}{\partial t} - \frac{\partial}{\partial x} \left(\theta D_k \frac{\partial C_k}{\partial x} \right) = (1 - \theta) F_k(C_1, \dots, C_N, S_p) \quad \forall k (1 \leq k \leq N) \quad (14)$$

where $F_k(C_1, \dots, C_N, S_p)$ is the molar rate of production of species k due to dissolution of the solid phases.

For resolution of the model, the concentrations of species present at equilibrium in the liquid phase are estimated from:

- the equilibrium between the solid phases and the contact solution,
- the condition of electroneutrality,
- the possible interactions between species present in the solution

The qualitative properties of the mathematical model were analysed [16] and a diagramme proposed [17]. In the case when only a single chemical element is considered in different forms in the solid or liquid phases (e.g. calcium), the model developed gives identical results to those obtained using the shrinking front model.

4.2.2. Application: case of release of two species

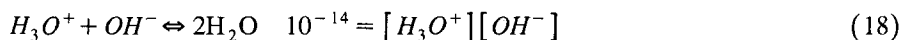
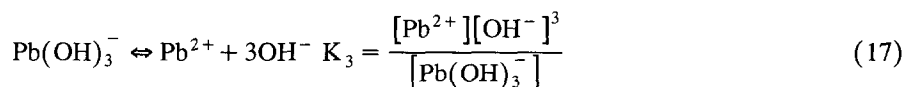
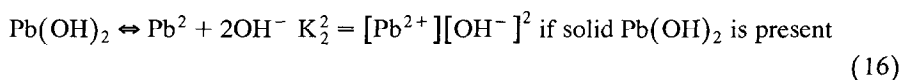
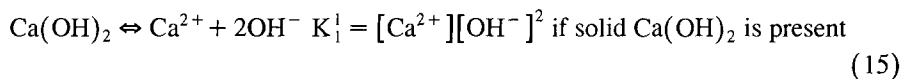
The model is studied for the case of a porous matrix with two components, calcium hydroxide and lead hydroxide.

Given that:

$$C_1 = [Ca^{2+}]; C_2 = [Pb^{2+}]; C_3 = [Pb(OH)_3^-]; C_4 = [OH^-]; C_5 = [H_3O^+]$$

$$S_1 = [Ca(OH)_2]; S_2 = [Pb(OH)_2]$$

The chemical equilibriums considered are:



The system to be resolved can be written:

$$\frac{\partial C_1}{\partial t} - D_1 \frac{\partial^2 C_1}{\partial x^2} = \frac{1 - \theta}{\theta} F_1(C_1, C_{\text{sat}_1}, S_1) \quad (19)$$

$$\frac{\partial C_2}{\partial t} - D_2 \frac{\partial^2 C_2}{\partial x^2} = \frac{1 - \theta}{\theta} F_2(C_2, C_{\text{sat}_2}, S_2) \quad (20)$$

$$\frac{\partial C_3}{\partial t} - D_3 \frac{\partial^2 C_3}{\partial x^2} = \frac{1 - \theta}{\theta} F_3(C_3, C_{\text{sat}_3}, S_2) \quad (21)$$

$$\frac{\partial S_1}{\partial t} = -F_1(C_1, C_{\text{sat}_1}, S_1) \text{ and } \frac{\partial S_2}{\partial t} = -F_2(C_2, C_{\text{sat}_2}, S_2) + F_3(C_3, C_{\text{sat}_3}, S_2) \quad (22)$$

with

$$F_1(C_1, C_{\text{sat}_1}, S_1) = \begin{cases} \alpha [C_{\text{sat}_1} - C_1] & \text{if } S_1 > 0 \\ 0 & \text{else} \end{cases} \quad (23)$$

$$F_2(C_2, C_{\text{sat}_2}, S_2) = \begin{cases} \alpha [C_{\text{sat}_2} - C_2] & \text{if } S_2 > 0 \\ 0 & \text{else} \end{cases} \quad (24)$$

$$F_3(C_3, C_{\text{sat}_3}, S_2) = \begin{cases} \alpha [C_{\text{sat}_3} - C_3] & \text{if } S_2 > 0 \\ 0 & \text{else} \end{cases} \quad (25)$$

Initial conditions

$$C_1(x, 0) = C_{0_1}(x); C_2(x, 0) = C_{0_2}(x); C_3(x, 0) = C_{0_3}(x) \quad (26)$$

$$S_1(x, 0) = S_{0_1}(x); S_2(x, 0) = S_{0_2}(x)$$

Boundary conditions

$$\frac{\partial C_1(1, t)}{\partial x} = 0; C_1(0, t) = C_{\text{interface}_1}$$

$$\frac{\partial C_2(1, t)}{\partial x} = 0; C_2(0, t) = C_{\text{interface}_2} \quad (27)$$

$$\frac{\partial C_3(1, t)}{\partial x} = 0; C_3(0, t) = C_{\text{interface}_3}$$

Chemical equilibria

$$K_1^1 = C_{\text{sat}_1} C_{\text{sat}_4}^2 \text{ if } 0 < S_1 \quad K_2^2 = C_{\text{sat}_2} C_{\text{sat}_4}^2 \text{ if } 0 < S_2 \quad (28)$$

$$K_3 = \frac{C_{\text{sat}_2} C_{\text{sat}_4}^3}{C_{\text{sat}_3}}; 10^{-14} = C_{\text{sat}_4} C_{\text{sat}_5} \quad (29)$$

$$C_{\text{sat}_5} + 2C_{\text{sat}_1} + 2C_{\text{sat}_2} = C_{\text{sat}_3} + C_{\text{sat}_4} \quad (30)$$

If for $1 \leq p \leq 2$, S_p disappears, then in the Eqs. (29) and (30), $C_{sat,p}$ is replaced by C_p solution of the Eq. (19), Eq. (20), or Eq. (21).

5. Validation of the model with chemical interactions

In order to verify that the coupled model dissolution/diffusion allows us to predict the intensity and dynamics of release, different simulations were carried out and compared to results obtained from leaching tests using demineralized water.

In Figs. 22 and 23, the interpretation of results of sequential leaching, according to the coupled model for block I r, is presented (logarithm of release flux J [$\text{kg m}^{-2} \text{s}^{-1}$] versus the logarithm of time [s]).

The values for the parameters used in the simulation are given in Table 6.

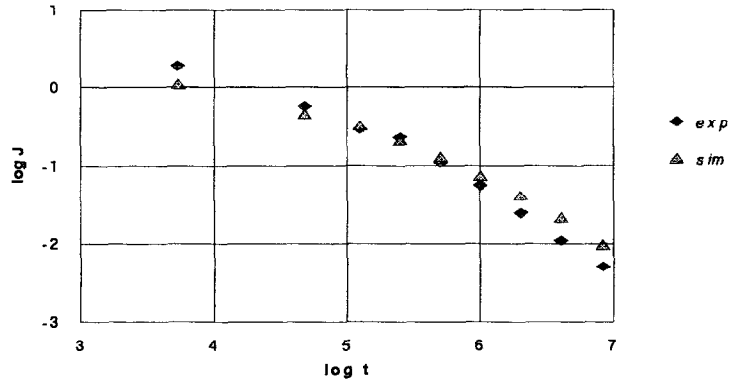


Fig. 22. Comparison of experimental flux of calcium and simulated flux using the coupled model dissolution/diffusion (Block I r).

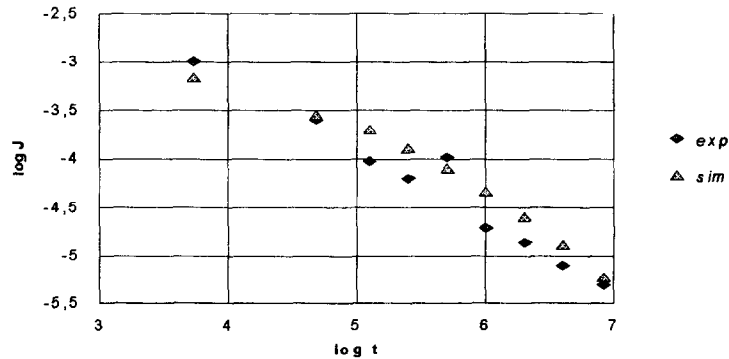


Fig. 23. Comparison of experimental flux of lead and simulated flux using the coupled model dissolution/diffusion (Block I r).

Table 6
Values of parameters of coupled model dissolution/diffusion, Block I r

θ (%)		45
Concentration of solid phases (kg m^{-3} of porous medium)	Ca(OH)_2	500
	Pb(OH)_2	1.9
Diffusion coefficients ($\text{m}^2 \text{s}^{-1}$)	Species Ca^{2+}	7×10^{-10}
	Species Pb^{2+}	7×10^{-10}
	Species Pb(OH)_3^-	7×10^{-10}
Product of solubility for lead: $[\text{Pb}^{2+}][\text{OH}^-]^2$		$10^{-18.2}$

The following observations can be made:

(1) The mean bulk diffusion of lead hydroxide was calculated from the initial quantity incorporated. The bulk diffusion of calcium hydroxide was estimated by considering that Ca(OH)_2 represents about 20% of the mass of the hydrated cement and that an important quantity of lime comes from the APC MSW.

(2) The porosity was estimated by the determination of the water absorption capacity (WAC), i.e., mass of water absorbed by dry mass of material [18].

(3) The diffusion coefficients used are of the same order (ca. $10^{-9} \text{ m}^2 \text{ s}^{-1}$) as those found in the literature [17] for Ca^{2+} and Pb^{2+} at infinite dilution.

(4) The products of solubility for lead hydroxide found in the literature vary from one author to another: $10^{-14.36}$ [19], 10^{-15} [20], 10^{-19} [21].

(5) The length of each period of leaching influences the form of the curves, as the pH changes with each renewal of leaching solution, which considerably modifies the solubility of lead. Figs. 24–26, obtained by simulation, show respectively the variation of pH in the leaching solution, the variation of pH in the region close to the liquid–solid interface and its effect on the solubility of lead.

(6) The model developed is monodimensional. Its application in the case when release occurs on all faces of the block remains valid as long as the core is not affected by release.

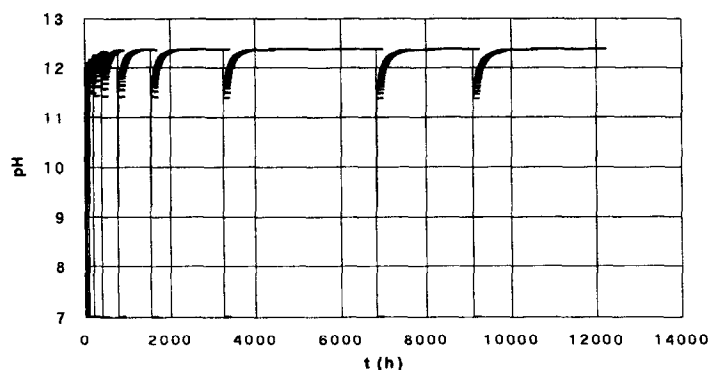


Fig. 24. Simulation of evolution of pH in the leaching solution.

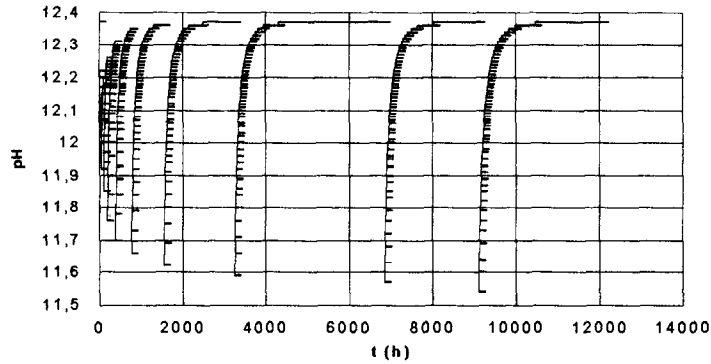


Fig. 25. Simulation of the evolution of pH near the solid-liquid interface.

(7) The simulation software only takes into account the form Ca^{2+} of calcium and the forms Pb^{2+} (preponderant species in an acidic solution), and $\text{Pb}(\text{OH})_3^-$ (preponderant species in a basic solution) of lead.

(8) The case of lead is specific: as long as lead in solid form is present in the zone near the surface of the block, the flux is according to the saturation concentration. It would seem that the release of lead is governed by a surface phenomenon. In this case, the model can be simplified. In fact, the calculation of the profile of lead concentration within the block is not necessary: it is only necessary to determine the concentration of lead at equilibrium in the surface zone; the flux can then be expressed in terms of a transfer coefficient of global mass, of the concentration at equilibrium and the concentration in the leaching solution. Fig. 25 shows the evolution of pH within the block in the zone near the solid/leaching solution interface. After each renewal of leaching solution, the pH increases from about 11.5 (this value decreases with time) to 12.3, which leads to a variation in lead solubility to a factor of 10 (Fig. 26).

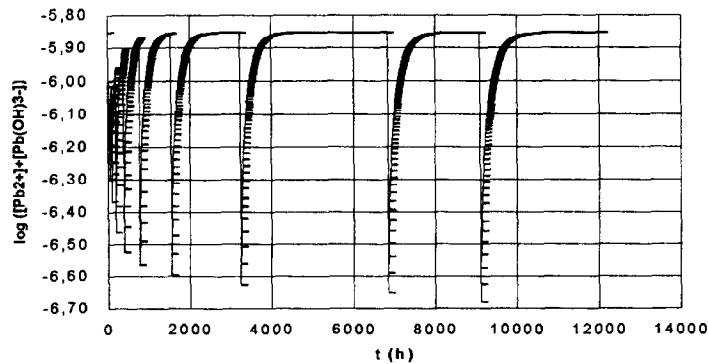


Fig. 26. Simulation of the evolution of lead solubility near the solid-liquid interface.

6. Conclusions

For highly soluble species, the simulation of leaching and optimal identification of parameters of the diffusional model for pollutant release are possible.

Three phases in the evolution of release during leaching can be observed:

(I) An initial phase, where surface phenomena and characteristics of each element are preponderant. For example, in the case of calcium, it can be supposed that fixing by carbonation on the surface zone in contact with air inhibits release at the beginning [1,6].

(II) A second phase, where release can be described by the diffusional model. This phase can be subdivided into:

(1) The period during which the behavior of the leached solute is described by the semi-infinite solid diffusional model. The length of this period is according to the block dimensions and the behavior of the element.

(2) The period when depletion of the solute in the block core begins. The flux of the solute begins to decrease more rapidly than predicted by the semi-infinite diffusional model. This difference allows simultaneous identification of the parameters C_0 and D_a of the diffusional model.

The apparent diffusion coefficients D_a identified by application of the diffusional model are to the order of $10^{-11} \text{ m}^2 \text{ s}^{-1}$. It can be considered that there is no great difference in kinetic behavior between the different species in the blocks.

The available release potential concentrations, C_0 , are generally lower than the total concentrations of the species in the blocks.

(III) The third phase observed during leaching tests is called 'residual' flux. During this phase, release continues although the diffusional flux defined in the previous phase has stopped. The value of the residual flux is in general 100 to 1000 times lower than the diffusional flux at the beginning of release.

A possible explanation of this phenomenon could be the continuation of release of a less soluble phase of the solid after depletion of the more soluble phase. In the case of calcium, we can imagine the continuation of release after depletion of portlandite, by solubilization of the calcium in the more stable phases of the product, CSH for example [1,6].

For amphoteric metals (e.g., lead), the set of results obtained shows the importance of chemical interactions of the pollutant and of the matrix, in particular, phenomena concerning solubilization/diffusional transport during leaching. Release is sensitive to the chemical context of the leaching solution and cannot, in general, be interpreted by the diffusional model.

Although the coupled dissolution/diffusion model is a simplification as regards the complex chemical system, constituted by the porewater of a cement matrix, it nevertheless seems to well represent, qualitatively, the results of leaching tests and allows us to put forward hypotheses concerning the main phenomena involved in mass transfer.

Acknowledgements

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and management, the Ministry of the Environment and ADEME (French Environmental and Energy Management Agency). Part of its works have been also presented in the framework of WASCON'94 [22].

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