

# Leaching behaviour of low level organic pollutants contained in cement-based materials: Experimental methodology and modelling approach

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## Abstract

The aim of this paper is the investigation of the leaching behaviour of different porous materials containing organic pollutants (PAH: naphthalene and phenanthrene). The assessment methodology of long term leaching behaviour of inorganic materials was extended to cement solidified organic pollutants. Based on a scenario-approach considering environmental factors, matrix and pollutants specificities, the applied methodology is composed of adapted equilibrium and dynamic leaching tests. The contributions of different physical and chemical mechanisms were identified and the leaching behaviour was modelled.

The physical parameters of the analysed reference and polluted materials are similar. A difference in the pore size distribution appears for higher naphthalene content. The solubility of the PAH contained in the material is affected by the ionic strength and by the presence of a co-solvent; the solution pH does not influence PAH solubility. The solubility of the major mineral species is not influenced by the presence of the two PAH nor by the presence of the methanol as co-solvent in the range of the tested material compositions.

In the case of the leaching of a monolith material the main transport mechanism is the diffusion in the porous system. For both mineral and organic species we observed at least two dynamic domains. At the beginning of the leaching process the released flux is due to the surface dissolution and to the diffusion of the main quantity dissolved in the initial pore solution. The second period is governed by a stationary regime between dissolution in pore water and diffusion. The model, coupling transport and chemical phenomena in the pore solution, at the monolith surface and in the leachate simulates satisfactory the release for both mineral and organic species.

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**Keywords:** PAH; Stabilization/solidification; Co-solvent; Leaching; Modelling

## 1. Introduction

The stabilisation/solidification (s/s) with hydraulic (cement, lime) or pozzolanic binders (ashes from coal combustion) is one of the favourite management issues for highly polluted inorganic waste, contributing to the environmental impact reduction by decrease of pollutants mobility and release. In France, about 600,000 tonnes of “ultimate” waste are yearly processed using cement based stabilisation/solidification [1]. Waste admissibil-

ity for s/s process is dependent on its low reactivity, particularly its content of organic matter (OM): French regulation stipulates that “ultimate” waste shall be exempt of OM. This criterion is restrictive for some of the major industries producing “ultimate” waste, for example incineration, combustion, etc.

The s/s of organic pollutants is the subject of a large number of scientific contributions. The major part concern polycyclic aromatic hydrocarbons (PAH) and phenol compounds [2–8] but also organic waste and/or polluted soils containing high organic content, particularly PAH [9–13]. The used binders are mixtures of cements with specific adsorbents: clays and modified clays, activated carbon [13–16]. The OM reduces s/s performances: influences on cement hydration/hardened process and structural

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### Nomenclature

$a_S$	specific surface area solid/liquid ( $\text{m}^{-1}$ )
$A, a$	coefficients in B-Dot activity model
$A_{\text{specimen}}$	external surface area of the specimen
$B, B^\circ$	coefficients in the B-Dot model
$c$	element concentration in pore water ( $\text{mol m}^{-3}$ )
$c'$	element concentration in the leachate ( $\text{mol m}^{-3}$ )
$D_e$	effective diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
$E$	void volume fraction
$2h$	monolith thickness (m)
$I$	ionic strength (molal)
$k$	dissolution/precipitation kinetic constant ( $\text{s}^{-1}$ )
$k_s$	surface dissolution kinetic constant ( $\text{s}^{-1}$ )
$k_{sO}$	dissolution intrinsic rate constant ( $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ )
$k_{SL}$	solid-to-liquid mass transfer coefficient ( $\text{m s}^{-1}$ )
$K_s$	solubility product
$s$	solid concentration in pore water ( $\text{mol m}^{-3}$ )
$s'$	solid concentration in leachate ( $\text{mol m}^{-3}$ )
$t$	time (s)
$V_{\text{leachate}}$	leachate volume ( $\text{m}^3$ )
$V_{\text{specimen}}$	specimen volume ( $\text{m}^3$ )
$x$	space coordinate (m)
$z$	ion charge
<i>Greek letters</i>	
$\gamma$	activity coefficient
$\delta$	thickness of the degraded surface
$\varepsilon$	dielectric constant
$\vartheta$	open porosity of the material
<i>Superscripts</i>	
'	related to the leachate
<i>Subscripts</i>	
exp	experimental
s	surface
sat	saturation
0	initial state

consequences on the formed materials depend on the content and characteristics of the organic species (e.g. acidic capacity, solubility) but the involved physical and chemical mechanisms are still not well known.

Limiting factors for a large application of cement based  $s/s'$  of organics are:

- the great variety of organic pollutants and
- their disturbance effect on cement hydration with
- negative consequences on mechanical and pollutants retention characteristics [17–20] of the new solid materials.

In consequence, alternative, more efficient treatment processes of organic pollutants are favoured.

In parallel, different organic admixtures are traditionally added in mortar or concrete composition for a better control of

cement hydration process or to get materials with specific properties [21,22]: plasticisers and superplasticisers, de-foaming agents, retarders, accelerators, air-entraining agents, water-proofing agents, grouting aids, stabilisers, etc. These technological additions are inserted at different times of the hardening process and in small quantities, generally less than 5% of the binder mass [18]. The composition of this organic addition, a mixture of natural and/or synthetic products is very variable and occasionally kept secret: ligno-, melamine-, naphthalene-sulphonates, different polymers, tributyl phosphate, silicon organic compounds, phenolic compounds, sucrose, gluconates, formats, natural and synthetic tensides: soaps, non-ionic and anionic tensides such alkyl-polyglycol ether, alkylaryl-polyglycol ether, alkylsulphates; fatty acids, cellulose ethers, bitumen emulsions, different esters like butyl stearate, and so on [14,19,20]. Most of the scientific literature in the field of admixture's use is dedicated to their influence on the hydration mechanisms and phases formation and on the properties of the concrete or mortar: many concrete properties cannot be achieved without concrete admixtures. Relatively few are the contributions dedicated to the evolution of additives after their insert: their conversion in the hardened cement paste and in the pore water, their environmental impact. In fact, the characteristics of the liquid phase (concentration, alkalinity) during hydration/hardening and in the pore system can lead to chemical conversion (for example by hydrolysis) of the admixtures and generate in this way potentially more mobile organic pollutants [23–25]. Zhang et al. [26] established that ligno- or naphthalene-sulphonates can be broken down in the liquid phase with different rates and products released by leaching. The results show that only a small part of the used admixtures can be eluted. Unfortunately too often the used assessment leaching tests are normalised as short compliance tests, for example 24 h of leaching in DEV S4 [25]. Therefore the methods are not adapted for the investigation of organic species transfer and transport mechanisms during leaching.

In this context it seemed useful to propose a methodology for the assessment of the behaviour of porous solid materials containing organic pollutants, disposed in an environmental scenario. The application of this methodology could also better address the issue of complete elimination of OM from the “ultimate” waste to be solidified with cement.

Based on our experimental and modelling experience in the field of leaching of inorganic species from cement based porous materials [27–30] an experimental program was performed for the investigation of the leaching behaviour of materials based on cement CEM I containing two commonly used PAH, naphthalene and phenanthrene.

The research program deals with the following objectives:

- to upgrade our methodology for the leaching behaviour assessment of porous cement-based materials by extending it from inorganic to organic pollutants,
- to describe the main mass transfer processes involved in organic species leaching and their influence on the leaching mechanism of inorganic species, and
- to model the organic and inorganic species leaching process for long term behaviour assessment.

Table 1  
Physical and chemical properties [31]

PAH	Number of cycles	Molecular weight (g/mol)	Solubility in water (mmol/L)	Vapour pressure (Pa)	Henry's constant (atm m <sup>3</sup> mol <sup>-1</sup> )	log <i>K</i> <sub>OW</sub>
Naphthalene	2	128	0.23	6.5	4.8 × 10 <sup>-4</sup>	3.37
Phenanthrene	3	178	0.0072	9.1 × 10 <sup>-2</sup>	8.6 × 10 <sup>-5</sup>	4.46

## 2. Materials and methods

### 2.1. Organic pollutants choice

The PAH organic contaminants used in this study, i.e. the naphthalene and phenanthrene, belong to the 16 most toxic PAH, as published by the US EPA. Their choice was determined by their physical and chemical properties (Table 1) such as a high volatility and water solubility (relative to the PAH family), a high toxicity and also for their occurrence in industrial wastes or polluted soils. In the anaerobic conditions of our leaching program PAH are considered to be unbiodegradable.

### 2.2. Stabilised/solidified materials

Four different material samples have been prepared: one reference material sample without any organic pollutant (named T), two material samples containing naphthalene at 1% and 5% mass fraction (named N1 and N5, respectively) and one material sample with 1% phenanthrene (named P).

The hydraulic binder used for all materials was the Ordinary Portland Cement (OPC) CEM I, NF EN 197-1 [32]. Based on a preliminary solidification program, the final solidification formula was selected. Each sample contained fine Fontainebleau silica sand (<1 mm) playing the role of an inert mineral waste. The ingredients were mixed in solid state, the solid PAHs being crushed below 1 mm. The stabilized/solidified specimens were prepared according to the experimental protocol of the European standard EN 196-1 [33]. Each formulation was prepared in 5 kg batches. Samples were cured for 28 days in a dark environment and kept at constant humidity and temperature (23 ± 2 °C).

The composition of the four materials is presented in Table 2.

### 2.3. Analytical methods

The target species monitored in the various characterization and leaching tests were inorganic ions as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and the two organics (naphthalene and phenanthrene).

The different eluates were filtrated on a polypropylene membrane of 0.45 μm porosity and the filtrates were acidified to pH 2 ± 0.5 with HNO<sub>3</sub> solution (65%). They were analysed for cations by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jobin Yvon Ultima 2). The detection limit was 0.385 mmol/L for Na<sup>+</sup>, 0.183 mmol/L for K<sup>+</sup> and 0.004 mmol/L for Ca<sup>2+</sup>. Anions like SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> were analysed by ion-chromatography (Dionex IC25). Organic contaminants (naphthalene and phenanthrene) were analysed by high performance liquid chromatography (HPLC, apparatus Shimadzu LC-6A and detector UV visible SPD-6A). The detection limit was 3.9.10<sup>-4</sup> mmol/L for naphthalene and 2.8.10<sup>-5</sup> mmol/L for phenanthrene.

### 2.4. Assessment methodology

The assessment methodology is based on a physico-chemical characterization of the materials and on leaching tests. The leaching behaviour was assessed according to the principles of the scenario approach ENV12920 [34]. The stabilised materials containing organic contaminants can contact leachates of various compositions, particularly relevant for this kind of materials being the case of leachates containing soluble organic matter. The soluble OM is acting as a co-solvent enhancing the solubility and the extractability of PAH. In this study the methanol was selected to play the role of soluble OM. Methanol is a common organic solvent forming a mono-phase liquid with water, without chemical reactivity and without complexing properties (for our experimental conditions).

Three leachates have been used: demineralised water (common leachate for inorganic species) and solutions of 5% or 10% (volume) methanol as co-solvent.

#### 2.4.1. Physical and chemical characterization of materials

The water adsorption capacity (WAC, %) [27], is determined by mass balance between the initial and final weight of the immersed sample submitted to the dynamic monolithic leaching test (DML, described below) and its total (soluble) release. The WAC allows calculation of the opened porosity.

Table 2  
Notation, composition and water/cement ratio of the materials

Notation	Pollutant	Weight (%)				W/C ratio
		Sand (S)	Cement (C)	Water (W)	Pollutant (P)	
T	None	55.00 ± 0.03	33.00 ± 0.02	12.00 ± 0.01	0.00	0.36
N1	Naphthalene	54.45 ± 0.03	33.35 ± 0.02	11.18 ± 0.01	1.02 ± 0.01	0.33
N5	Naphthalene	50.48 ± 0.03	33.34 ± 0.02	11.20 ± 0.01	4.98 ± 0.01	0.34
P	Phenanthrene	53.60 ± 0.03	32.87 ± 0.02	12.54 ± 0.01	0.99 ± 0.01	0.38

The apparent porosity and the pore size distribution were determined through mercury intrusion porosimetry, performed on small-drilled cores. Testing was performed on Micromeritics mercury porosimeter having a pressure range from sub-ambient to 400 MPa.

The total organic content was determined by solid/liquid extraction with methanol and analysis as specified in Section 2.3. The inorganic total content was determined by acid mineralization ( $\text{HNO}_3 + \text{HCl}$ ) of the samples and ICP-AES.

PAH solubilities in different solutions containing 5% and 10% (volume) methanol has been determined. For the same methanol concentration three kinds of solvents were used:

- deionised water,
- solution obtained after 7 days contact of demineralised water with monolithic reference material T (see DML protocol below), liquid/surface =  $10\text{m}^3/\text{m}^2$
- solution obtained after 7 days contact of demineralised water with crushed reference material T (see ANC protocol below) liquid/solid = 10 L/kg.

#### 2.4.2. Solid/liquid transfer properties

Two kinds of experiments were performed: a solid/liquid equilibrium test—the acid neutralisation capacity test (ANC) and the dynamic monolithic leaching test (DML). All leaching experiments were performed in duplicate, at ambient temperature ( $23 \pm 2^\circ\text{C}$ ) and in darkness. Glass vessels with caps fitted with Teflon seals were used to prevent adsorption of organic pollutants. The glass vessels were hermetically closed to prevent carbonation (alkaline leachates) and water and/or organic species evaporation. For all leaching tests the analysed target species were naphthalene, phenanthrene, Na, K, Ca,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ .

**2.4.2.1. ANC test.** The acid neutralisation capacity test was based on the methodology of the European standard prEN14429 [35]. The aim of the ANC test is to assess the pH influence on species solubility and acid neutralisation capacity of the material. For solid/liquid equilibrium characterization solids are crushed below  $<1\text{ mm}$ . In parallel 10 small batch reactors with the same liquid/solid ratio (10 mL/g dry material) are tumbled end over end for 7 days. The quantity of nitric acid (not complexing and only slightly oxidizing in our experimental con-

ditions) added in each solution is different in order to obtain final pH values in a wide range (3–13) [27]. After filtration, the solutions were analysed and results plotted to obtain the acid neutralization capacity of the materials (pH against acid amount, mequiv  $\text{H}^+/\text{g}$  dry material) and species solubilities (concentrations, mmol/L, against pH).

**2.4.2.2. DML test.** The DML test allows characterization of the dynamic release of species from monolithic blocks of material (in our case blocs of  $4\text{ cm} \times 4\text{ cm} \times 4\text{ cm}$ ). It is a batch test with periodical total renewal of the leachate, inspired by the tank leach test NEN 7345 (NNI, 1994) [36]. The liquid/surface ratio of  $10\text{ m}^3/\text{m}^2$  is maintained constant for each leachant renewal. The time intervals are chosen such that the concentrations of contaminants in the leachate remain under the solubility limits. Leachates were demineralised water or methanol solutions (5% or 10%). After separation, the solutions were analysed and results were used to plot the time depending properties and to assess the released molar fluxes of the different species ( $\text{mmol}/\text{m}^2\text{ s}^{-1}$ ).

### 3. Experimental results and discussions

#### 3.1. Physical and chemical characterisation of materials

The physical properties and the analysed total content of the materials are presented in Table 3. Values of parameters are similar for the reference material T and the materials containing small quantities of pollutants, N1 and P.

Two distinct procedures were used and compared for connected open porosity assessment. Generally, water porosity determined at the end of the DML test is 1.5 times higher than the initial porosity of samples measured by Hg intrusion porosimetry. Pore diameter distributions are similar for T, P and N1; N5 material shows a relative high value for  $1\text{ }\mu\text{m}$  pores incidence (Fig. 1). The material N5, containing more volatile naphthalene does not show the same proportion for the water porosity/mercury porosity of about 1.5. In fact, “traditional” Hg porosimetry seems not sufficiently adapted for materials containing (high) volatile compounds, like naphthalene. Therefore we decided to use water porosity values for leaching modelling.

Table 3  
Physical properties and composition of the materials

	Materials			
	T	N1	N5	P
Density ( $\text{kg}/\text{m}^3$ )	$2.1 \pm 0.1$	$2.1 \pm 0.1$	$2.0 \pm 0.1$	$2.11 \pm 0.05$
WAC (%)	$8.53 \pm 0.01$	$8.30 \pm 0.04$	$9.14 \pm 0.01$	$8.9 \pm 0.1$
Water porosity (%)	$17.7 \pm 0.4$	$17.9 \pm 0.4$	$17.8 \pm 0.4$	$18.9 \pm 0.4$
Porosity (%) by Hg	$11.5 \pm 0.6$	$12.4 \pm 0.1$	$18.1 \pm 0.8$	$12 \pm 2$
Total content (mg/kg, uncertainty of 5%)				
Organic	–	11423	36548	8206
Ca	170550	170049	169835	164403
Na	1187	1929	1335	1410
K	3487	3900	3653	3487

Table 4  
Solubility of naphthalene in methanol solutions (23 °C)

Naphthalene solubility (mmol/L) in presence of	Solution		
	Deionised water	Solution from contact with monolithic T	Solution from contact with crushed T
5% of methanol	0.28	0.22	0.25
10% of methanol	0.40	0.28	0.33

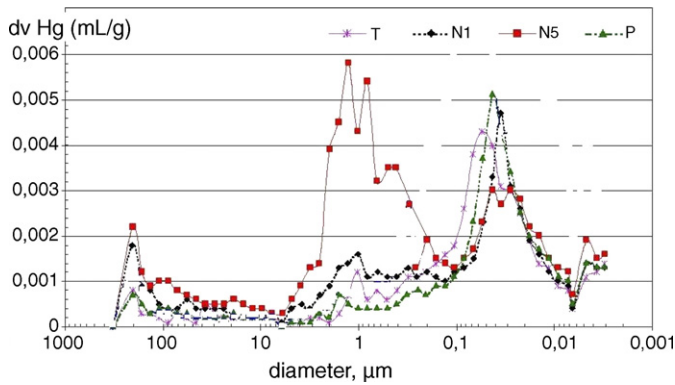


Fig. 1. Hg porosimetry of the four materials: incremental Hg volume vs. pore diameter.

The PAH solubility is a model input parameter. Its experimental values are obtained for 5% and 10% methanol solutions in which solvent is demineralised water and respectively solutions containing soluble salts released by the reference material T. Solubility results obtained with a uncertainty of 5% are presented in Table 4. PAH solubility increases with methanol content (0.23 mmol/L for naphthalene in water, Table 1) but decreases with the increase of the ionic strength of the solutions in contact with the material (Table 4).

### 3.2. Solid/liquid transfer properties

Concerning the ANC test the four materials have a high alkaline power (pH of 12.6). The buffering capacity seems to be slightly higher for the reference material proving an influence of OM content on the cement hydration process (Fig. 2).

Mineral species have a “classical” pH dependent solubilization commonly observed in the pH range from 3 to 13 in the case of different wastes s/s with OPC [28–30]. For this reason,

the graphical results are not presented here. So, for all materials we observed:

- A pH independent solubility for species considered as non-reactive, like alkaline ions and chloride. The solubility level is also independent on the total organic content of the material.
- A pH dependent solubility for other species like Ca which concentration decreases from 375 mmol/L in acidic medium to 20 mmol/L at pH 12.6 and  $\text{SO}_4^{2-}$  which solubility decreases from 6.5 mmol/L at pH 3 to 0.04 mmol/L at pH 12.6. This behaviour is characteristic of a solubilization process controlled by portlandite for Ca and ettringite for  $\text{SO}_4^{2-}$  [28–30].

Naphthalene’s solubility (0.18 mmol/L) in these highly concentrated solutions is lower than in pure water. It is practically pH independent in the range of pH 3–13 and also independent on the naphthalene total content in the solid material. Consequently the eluates are supposed to be saturated (Fig. 2). On the other hand phenanthrene solubility remains close to its water solubility at acidic pH values and slightly increases when pH becomes Basic (Fig. 2).

The species release in the case of DMLT was modelled; the experimental results of DMLT are compared with simulations in the next chapter. The different assays performed are named by the material symbol followed by the co-solvent composition. For example N5co10: material N5 leached with 10% co-solvent solution.

## 4. Leaching behaviour modelling

A leaching behavioural model for solidified/stabilized porous materials containing organic compounds was developed and applied in the conditions of the dynamic tests. This model was intended to describe the major physico-chemical interactions and mass transfer phenomena of species having typical

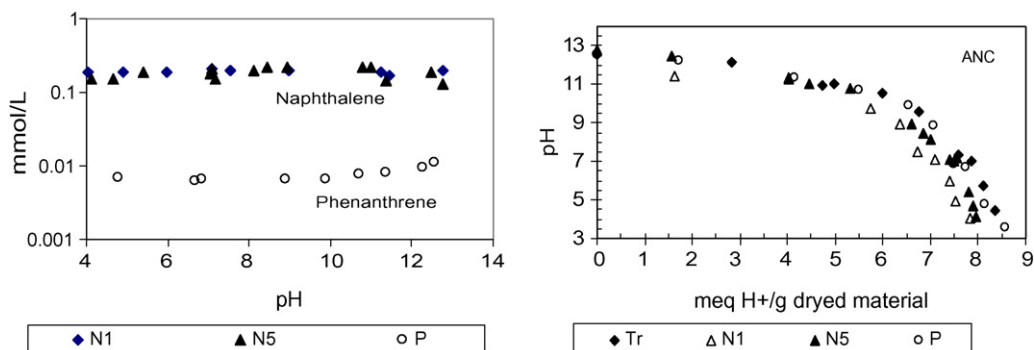


Fig. 2. Organics solubility vs. pH and ANC of all studied materials.



behaviours: (i) major elements contained in mineral phases and determining the pH and the ionic strength of the pore-water and leachate (Na, K and Ca) and (ii) organic pollutants. The reciprocal influence of organic compounds and minerals on leaching behaviour was studied.

When the material is immersed in water, two reaction compartment will form: the pores system of the material and the leachate compartment. The pores system is the place of dissolution/precipitation, acid/base, complexation, redox, etc. reactions. The different soluble chemical species diffuse through the pores from the material core to the leachate. The changes in pore-water composition due to diffusion may affect the solubility of the different solid phases. The surface of the material is in contact with the leachate which is an aggressive solution whose composition is generally very different from that of the pore-water (leachate initial pH  $\leq 7$  when pore solution pH  $\geq 13.6$ ). Therefore a dissolution process and other reactions can occur at the leachate/samples interface.

For the studied material prepared with a hydraulic binder, the acid/base, complexing and precipitation/dissolution reactions determine the main mineral speciation in the pore water and leachate. A simplified mineral chemical model was adopted, able to explain the major mineral's behaviour and to allow the organic-mineral interaction study.

Calcium in the eluate comes mainly from portlandite dissolution. Calcium silicate hydrates are not considered in the leaching model because they are less soluble than portlandite and their dissolution occurs after portlandite depletion in the solid matrix [37].

Na<sup>+</sup> and K<sup>+</sup> are well-known for their chemical stability in solution and for their high solubility. However a residual flux has been observed experimentally for long term leaching. This two step release may be explained by the presence of solid mineral phases of different solubilities: (i) the most soluble are dissolved at the initial contact with water and the formed ions diffuse towards the leachate and (ii) weak soluble silicates are responsible for the observed residual flux.

After the release of the initially soluble elements (mainly alkaline elements), the pore water composition remains more stable until depletion of portlandite which occurs at very long term for this kind of materials.

The other mineral species monitored during the experimental program such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> are at very low concentrations in the pore water and do not affect the behaviour of the other species to any significant extent as far as modelling is concerned here.

The organic compounds can be found as precipitated, adsorbed phases and in solution. The adsorbed fraction of hydrophobic organic compounds on hydrated silicates or quartz is considered negligible with regard to the precipitated phases and to the important total content of these compounds in the studied materials. This hypothesis is based on the experimental results of ANC test in which the solubilization of naphthalene was found independent of the naphthalene total content in the material. Consequently the precipitation/dissolution and diffusion are the main process considered to explain the organic compound behaviour.

#### 4.1. Model equations

To model the dissolution/precipitation process for mineral species a simple first order equation is used:

$$\begin{aligned} \frac{\partial s}{\partial t} &= k(c - c_{\text{sat}}) \quad \text{if } (s > 0) \text{ or } ((s = 0) \text{ and } (c \geq c_{\text{sat}})) \\ \frac{\partial s}{\partial t} &= 0 \quad \text{if } (s = 0) \text{ and } (c < c_{\text{sat}}) \end{aligned} \quad (1)$$

where  $s$  is the solid concentration,  $c$  the aqueous species concentration and  $k$  is the kinetic constant. The saturation state  $c_{\text{sat}}$  is calculated from the thermodynamic equilibrium constants, expressed with ion activities in the case of mineral species. To calculate ionic activities the B-Dot activity model is used. It is an improved Debye-Hückel model [38] allowing calculations for ionic strengths up to 1 m ( $I < 1$  m in this study):

$$\log \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + a_i B\sqrt{I}} + B^\circ I \quad \text{and} \quad I = 0.5 \sum c_i z_i^2 \quad (2)$$

where  $I$  is the ionic strength,  $A$  and  $B$  are constants. For pure water  $A = 0.5092$ ,  $B = 0.3283$ ,  $B^\circ = 0.04$  at 25 °C,  $a_i$  being the ion size parameter for each species.  $I$  varies from 0.001 to 0.01 for all analysed DMLT leachates and is estimated to be close to 0.5 for the pore water ( $L/S = 0.08$  l/kg and considering the soluble elements in the pore water).

The electroneutrality condition completes the description of the aqueous phases:

$$\sum c_{+z_{+}} = \sum c_{-z_{-}} \quad (3)$$

where (+) is the symbol for all cations including H<sup>+</sup> and (−) for all anions including OH<sup>-</sup>.

The hypothesis of local equilibrium is considered for the reactions occurring in the aqueous phase and for the dissolution/precipitation reactions in the pore water (chemical process are faster than diffusion).

The equilibrium and kinetic relations and the activity model apply in the same way to the pore-water and the leachate (superscript ' for all leachate parameters).

In the porous matrix, the evolution of the pore-water concentration for a given species is the result of diffusion and dissolution/precipitation:

$$\vartheta \frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} - \vartheta \frac{\partial s}{\partial t} \quad (4)$$

where  $D_e$  is the effective diffusion coefficient of the considered species and  $\vartheta$  is the material open porosity. The one-dimensional diffusion equation is used for an equivalent sheet of thickness  $2h = \text{specimen volume/surface}$ ,  $0 \leq x \leq h$ . The boundary conditions are:

- in the center of the material ( $x = 0$ ):

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = 0$$

- at the leachate/material interface ( $x = h$ ):

$$D_e \left. \frac{\partial c}{\partial x} \right|_{x=h} = k_{SL}(c' - c|_{x=h}) \quad (5)$$

where  $k_{SL}$  (m/s) is the mass transfer coefficient between the eluate and the pore-water at the surface of the material.

The leachate composition is determined by the mass flows from the pores (diffusion), the surface dissolution of the material and chemical reactions in the liquid phase. The leachate compartment is considered as a closed perfectly stirred tank reactor. The balance equation for each species in the eluate is:

$$\frac{dc'}{dt} = -\frac{1-E}{E} a_S k_{SL}(c' - c|_{x=h}) - \frac{\partial s'}{\partial t} - \frac{\partial s_s}{\partial t} \quad (6)$$

where  $c'$  is the leachate concentration and  $s'$  is the leachate concentration of a solid phase (precipitation may occur in the leachate) with a precipitation/dissolution kinetic equation of type (1). The specific solid/liquid exchange surface  $a_S$  and the leachate volume fraction  $E$  are defined by:

$$a_S = \frac{A_{\text{specimen}}}{V_{\text{specimen}}} \quad (7)$$

$$E = \frac{V_{\text{leachate}}}{V_{\text{leachate}} + V_{\text{specimen}}} \quad (8)$$

Many laboratory observations [29,30,39] strengthen the hypothesis that a thickness  $\delta$  of material is rapidly partially degraded during the first 1000 h of leaching by the solubilization of most easily soluble phases. A first order kinetics was experimentally observed for the dissolution of calcium. It can be noted that this surface phenomenon is different from that observed in the very long term [40,41] which is due to degradation of all the hydrated phases containing calcium. A first order kinetic equation has been used to describe the mineral dissolution in the surface layer  $\delta$ , characterized by a kinetic constant  $k_s$  and a limited concentration  $c'_{\text{sat}}$  with respect to the leachate composition:

$$\begin{aligned} \frac{\partial s_s}{\partial t} &= k_s(c' - c'_{\text{sat}}) \quad \text{if } (s_s > 0) \text{ or } ((s_s = 0) \text{ and } (c' \geq c'_{\text{sat}})) \\ \frac{\partial s_s}{\partial t} &= 0 \quad \text{if } (s_s = 0) \text{ and } (c' < c'_{\text{sat}}) \end{aligned} \quad (9)$$

In the case of organic compounds the release kinetics is different from a first order one and, following the experimental observations, seems to be dependent on the quantity of each compound. In fact, the quantity of the organic compound is a measure of the crystal's surface area which represents a common kinetic parameter for the dissolution of most solids. A model taking into account the quantity of solid (proportional to the surface area of the crystals) was adopted for the dissolution of organic

compounds contained in the surface layer:

$$\begin{aligned} \frac{\partial s_s}{\partial t} &= k_{sO} s_s (c' - c'_{\text{sat}}) \quad \text{if } (s_s > 0) \text{ or } ((s_s = 0) \text{ and } (c' \geq c'_{\text{sat}})) \\ \frac{\partial s_s}{\partial t} &= 0 \quad \text{if } (s_s = 0) \text{ and } (c' < c'_{\text{sat}}) \end{aligned} \quad (10)$$

$k_{sO}$  is a intrinsic rate constant.

The set of Eqs. (1)–(10) was solved using the finite differences method. An explicit formula was used for  $x$ -coordinate and a numerical differentiation formula with variable steps for the time-coordinate (the Gear method). In the case of PAH the model may be decoupled and resolved separately for minerals and organics because no significant chemical interaction occur between them (see below the salting out effect and the co-solvent effect on mineral's solubility).

#### 4.2. Model parameter identification

The model contains some physical–chemical parameters available from the literature or from experimental measurements and other which have to be assessed by fitting the model to the experimental leaching data (Table 5). Calcium solubility is calculated from the solubility constant of portlandite in function of pH. Two parameters are expected to modify the solubility of the organic compounds: the salinity of the aqueous solutions and the co-solvent. The salting out effect on hydrophobic organic compound solubility has been studied and modelled [32] for the main seawater constitutive salts. However no data are available for very basic solutions like the pore water of cement-based matrix. Organic compound solubilities  $c_{\text{sat}}$  and  $c'_{\text{sat}}$  are available from the solubility measurements performed in this study in different solvents (Tables 1 and 4, ANC results).

The initial concentration values (the initial conditions of the model)  $c_0$  and  $s_0$  are available from the equilibrium tests and/or from the total content of elements in the material. The initial solid quantity in the reactive surface layer ( $s_{s0}$ ) is calculated from:

$$s_{s0} = s_0 \frac{\vartheta A_{\text{specimen}} \delta}{V_{\text{leachate}}} \quad (11)$$

Other parameters such as the dissolution kinetic constants  $k$  and the material/leachant transfer coefficients  $k_{SL}$  are evaluated with the hypothesis of local equilibrium (rapid reactions) in the porous system and rapid external mass transfer, respectively; their values are sufficiently high and do not modify the evolution of the concentrations of species.

Leachate concentrations of released species,  $c'_{\text{exp}}$ , were experimentally monitored versus time (concentration error less than 5%). Comparison of the calculated values of concentration  $c'$  with available experimental data  $c'_{\text{exp}}$  allowed adjustment of the unknown parameters, i.e.  $D_e$  for all monitored species,  $c_{\text{sat}}$  for the late dissolution of Na and K,  $k_s$ ,  $k_{sO}$  and  $\delta$ .

The effect of co-solvent on the solubility of minerals was estimated. The methanol diminishes the dielectric constant of water and then can modify the ion activities. This effect may be taken into account in the Davies activity model through the  $A$

Table 5  
Values of the physical–chemical parameters of the leaching model

Initial concentrations in pore water	mol m <sup>-3</sup>		Initial concentrations in leachate	mol m <sup>-3</sup>	
<i>c</i> <sub>Na 0</sub>	140		<i>c</i> ' <sub>Na 0</sub> ; <i>c</i> ' <sub>K 0</sub> ; <i>c</i> ' <sub>Ca 0</sub>	0	
<i>c</i> <sub>K 0</sub>	120		<i>s</i> ' <sub>Ca 0</sub> ; <i>s</i> ' <sub>Na 0</sub> ; <i>s</i> ' <sub>Na 0</sub>	0	
<i>s</i> <sub>Na 0</sub> <sup>a</sup>	640		<i>c</i> ' <sub>Naphthalene 0</sub> ; <i>c</i> ' <sub>Phenanthrene 0</sub>	0	
<i>s</i> <sub>K 0</sub> <sup>a</sup>	940		<i>s</i> ' <sub>Naphthalene 0</sub> ; <i>s</i> ' <sub>Phenanthrene 0</sub>	0	
<i>s</i> <sub>Ca 0</sub>	20000				
<i>c</i> <sub>Ca 0</sub> ; <i>c</i> <sub>Naphthalene 0</sub> ; <i>c</i> <sub>Phenanthrene 0</sub>	0				
<i>s</i> <sub>Naphthalene 0</sub>	1174 (N1); 3754 (N5)				
<i>s</i> <sub>Phenanthrene 0</sub>	555				
Fixed value parameters					
<i>k</i> (s <sup>-1</sup> )					1
<i>k</i> <sub>SL</sub> (m s <sup>-1</sup> )					1
Adjusted parameters for minerals					
<i>c</i> <sub>sat Na</sub> (mol m <sup>-3</sup> )					0.55
<i>c</i> <sub>sat K</sub> (mol m <sup>-3</sup> )					0.12
<i>D</i> <sub>e Na</sub> (m <sup>2</sup> s <sup>-1</sup> )					3.0 × 10 <sup>-12</sup>
<i>D</i> <sub>e K</sub> (m <sup>2</sup> s <sup>-1</sup> )					4.5 × 10 <sup>-12</sup>
<i>D</i> <sub>e Ca</sub> (m <sup>2</sup> s <sup>-1</sup> )					5.0 × 10 <sup>-12</sup>
$\delta$ (m)					250 × 10 <sup>-6</sup>
<i>k</i> <sub>s, Ca</sub> (s <sup>-1</sup> )					3 × 10 <sup>-9</sup>
<i>k</i> <sub>s, Na, K</sub> (s <sup>-1</sup> )					1
	N1 water	N1 cosolvent	N5 water	N5 cosolvent	
Adjusted parameters for organics					
<i>D</i> <sub>e Naphthalene</sub> (m <sup>2</sup> s <sup>-1</sup> )	4 × 10 <sup>-12</sup>	4 × 10 <sup>-12</sup>	2 × 10 <sup>-11</sup>	3 × 10 <sup>-11</sup>	
$\delta$ (m)	150 × 10 <sup>-6</sup>	250 × 10 <sup>-6</sup>	150 × 10 <sup>-6</sup>	250 × 10 <sup>-6</sup>	
<i>k</i> <sub>sO</sub> (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	3 × 10 <sup>-6</sup>	6 × 10 <sup>-6</sup>	3 × 10 <sup>-6</sup>	6 × 10 <sup>-6</sup>	
				P water	
Adjusted parameters for organics					
<i>D</i> <sub>e phenanthrene</sub> (m <sup>2</sup> s <sup>-1</sup> )				3 × 10 <sup>-12</sup>	
$\delta$ (m)				150 × 10 <sup>-6</sup>	
<i>k</i> <sub>sO</sub> (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )				3 × 10 <sup>-4</sup>	

<sup>a</sup> For Na and K: *s*<sub>0</sub> + *c*<sub>0</sub> = total content.

and *B* constants [42]:

$$A = \frac{1.82 \times 10^6}{(\varepsilon T)^{3/2}} \quad \text{and} \quad B = \frac{50.3}{(\varepsilon T)^{1/2}} \quad (12)$$

*T* is the temperature and  $\varepsilon$  is the dielectric constant of the mixture which can be calculated as:

$$\varepsilon = \sum \varepsilon_i f_{v,i} \quad (13)$$

where *f<sub>v</sub>* are the volume fractions of solvent and water,  $\varepsilon_{\text{water}} = 78.5$  and  $\varepsilon_{\text{methanol}} = 32.6$ . For the two co-solvent solutions used in this study, 5% and 10% methanol,  $\varepsilon$  is 76.2 and 73.9, respectively. For the 10% methanol solution, *A* = 0.557 and *B* = 0.338, values which are very close to pure water constants *A* and *B*. Consequently, no significant co-solvent effect on mineral's solubility is expected.

The experimental solubilities of naphthalene in 5% and 10% methanol solutions were used (Table 5).

## 5. Modelling results and discussion

The figures below present measured and simulated flux of the monitored mineral and organic species versus leaching time. The leachate pH evolution is also shown. As a general observation, two kinetic domains occur for all species: a first period during about 2000 h when the flux decreases rapidly and a long term domain when the flux remains constant.

### 5.1. Case of minerals

Alkalines exhibit the same leaching behaviour, hence only Na is presented below. The same flux was observed for all materials (T, N, P) and leachants used (demineralised water, co-solvent) meaning that no effect of organic pollutant or co-solvent composition (between the limits of the studied concentrations) was observed on the behaviour of Na or K. Consequently the same estimated values for the model parameters, *c*<sub>sat</sub>, *D*<sub>e</sub>,  $\delta$ , *k*<sub>s</sub> (Table 5) were obtained for all leached materials. Fig. 3 shows that no distinction can be made between the different materials and leachates used in the test and consequently between the simulated fluxes.



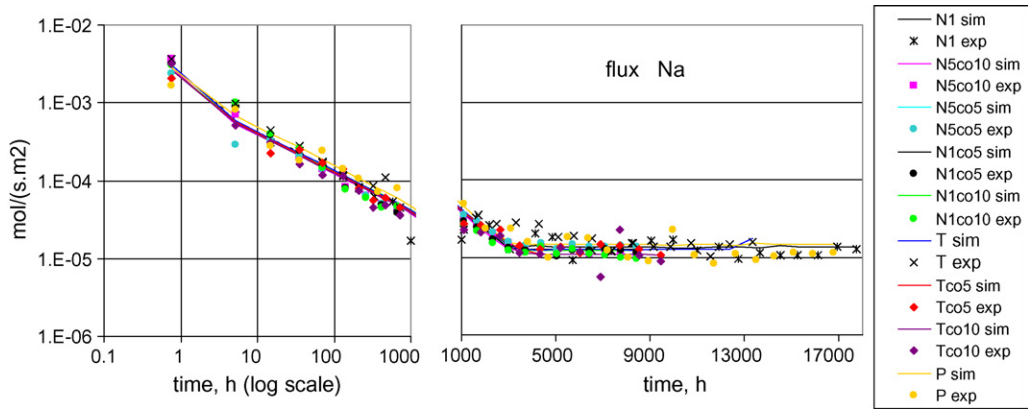


Fig. 3. Released flux of Na, simulation and experimental results.

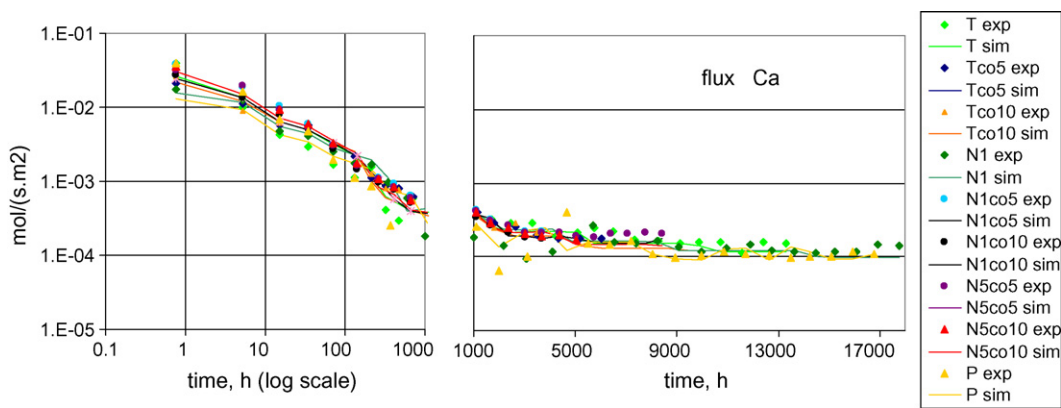


Fig. 4. Released flux of Ca, simulation and experimental results.

During the first 3000 h of leaching the main solubilized quantity of alkalines was entirely released by a diffusion controlled process (slope  $-0.5$ ). The first experimental point showing a faster initial release was simulated considering the instantaneous dissolution of Na and K contained in the superficial layer  $\delta$ . The dissolution of weak soluble phases containing Na (K) giving rise to a constant residual release became significant after this first period.

Experimental data show the same calcium behaviour for all materials and leachants (Fig. 4). The modelling results are in agreement with this conclusion because the model fitted param-

eters  $D_e$ ,  $\delta$  and  $k_s$  became the same values for all leached samples. The addition of methanol up to 10% as well as the presence of PAH have no significant effect on the solubility of portlandite.

Surface dissolution has a very important impact on calcium concentration as soon as the sample comes into contact with water and until about 1000 h of leaching. After this period the diffusion through porous system of the solubilized calcium becomes the main transport phenomenon and the flux is limited by the solubility value.

The pH simulation results are in good agreement with experimental data for all samples (Fig. 5). The eluate pH is calculated

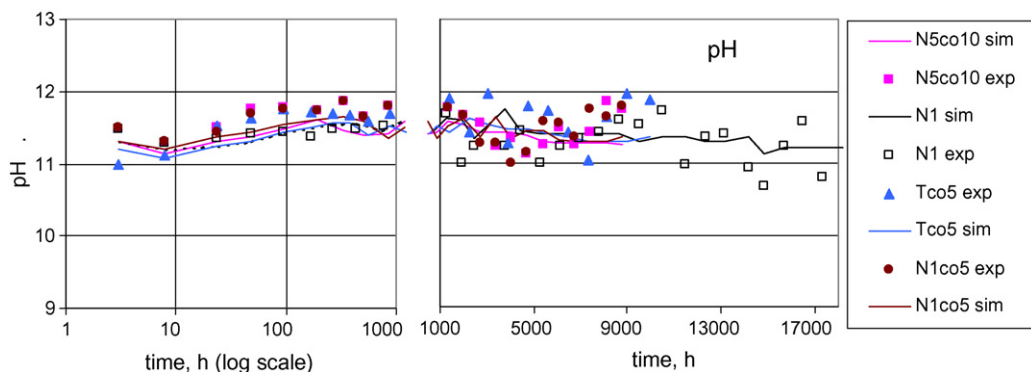


Fig. 5. Leachate pH, simulation and experimental results.

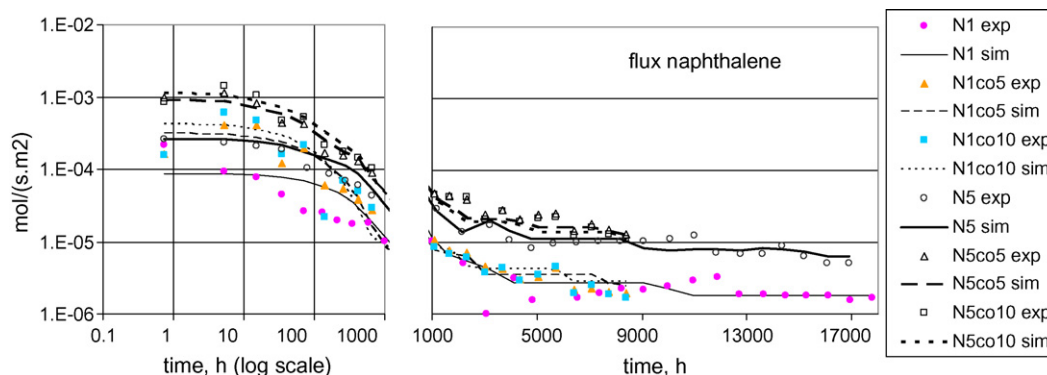


Fig. 6. Released flux of naphthalene, simulation and experimental results.

in the model from the electroneutrality equation and then it takes into account all the chemical phenomena during leaching as it depends on all species concentrations. In this way, the simulation of the pH evolution represents a global validation of the model.

## 5.2. Case of organic compounds

For the first period up to 1000 h (Fig. 6) the released naphthalene flux is mainly due to the surface dissolution. The parameter characterizing the intensity of this phenomenon is the kinetic constant  $k_{sO}$  which has the same value for all materials leached with demineralised water and which is two times greater in the case of co-solvent leachant. The experimental data (Fig. 6) show that the initial flux depends on the initial content of naphthalene in the material, i.e. the initial flux for N5 samples is higher than for N1 samples. The model well simulates this fact. For this first period, the curve for N1 sample has a different shape and the simulation is not quantitative. An experimental artefact (for example the partial volatilisation of naphthalene) or an inhomogeneous sample surface can be the reason.

The second period is characterized by a one order of magnitude decrease of the released flux. The lower flux corresponds to the lower naphthalene content in the materials (N1) and the 10 times higher flux correspond to N5 samples. For this leaching period the dissolution and diffusion through the porous system are the main release mechanisms. The estimated diffusion coef-

ficients, which are 10 times higher for N5 samples than for N1, are in agreement with the experimentally observed behaviour and may be justified by the porous structure of the materials. A comparative study of the porosimetry results shows that the N5 material contains larger pores than the others for a total open porosity close to 0.17 for all materials (Fig. 1). The mean pore radius corresponding at the maximum porous volume is  $1 \mu\text{m}$  for N5 and  $0.04 \mu\text{m}$  for the others and we suppose that this macro porosity was created by the presence of hydrophobic PAH micro crystals. Consequently a multi-step diffusion process may be considered: (i) firstly the diffusion through the macro porosity of the most quantity of PAH takes place—this period was observed experimentally and (ii) secondly a smaller flux through the micro porosity may be expected at long term—not studied.

When compared with demineralised water leaching, a weak enhancement of the naphthalene flux may be observed (especially at the beginning of the leaching test) for the samples leached with co-solvent which is certainly due to the different naphthalene solubility values in these solvents (Fig. 6).

Phenanthrene containing material exhibits the same leaching behaviour as the naphthalene low-content material. This behaviour is in agreement with the similar porous structure of both materials and the physical–chemical mechanisms supposing to govern the release of these compounds (dissolution and diffusion). Fig. 7 shows a satisfactory agreement between the experimental and simulated flux of phenanthrene.

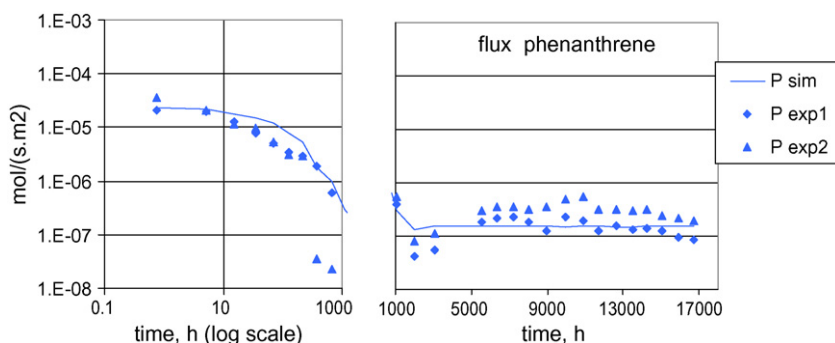


Fig. 7. Released flux of phenanthrene, simulation and experimental results.

## 6. Conclusions

The existing assessment methodology for long term leaching behaviour was extended to the problematic of the mobility of organic pollutants solidified within porous materials based on cement. The physical parameters of the analysed reference and “polluted” materials are similar. A difference in the pore size distribution appears for high naphthalene content.

The “classical” physical–chemical characterization of materials containing stabilized/solidified wastes has to be coupled with the long term environmental assessment in their target environment, so called scenario-approach. Adapted methodologies take into account the environmental factors and the specificities of the matrix and of the solidified pollutants. Environmental mobility assessment of organic pollutants requires adapted equilibrium and dynamic leaching tests and leaching conditions: time, temperature, leachate composition, presence of soluble organic matter.

The role of different physical–chemical mechanisms was identified and the material leaching behaviour was modelled. The solubility of the PAH contained in the material is affected by the ionic strength of the solution and by the presence of a co-solvent; the solution pH does not influence the solubility. The major mineral species release from an organic spiked material behaves like in the case of a common cement-based material. The solubility of the major mineral species is not influenced by the presence of the two PAH in the limits of their total content studied here (below 5%) nor by the presence of the methanol as co-solvent for concentrations below 10%.

In the case of a monolith leaching, the main transport mechanism is diffusion in the porous system. At the monolith surface a dynamic dissolution process was assumed and confirmed by modelling. Globally, for both mineral and organic species we observed at least two dynamic domains. At the beginning of the leaching process the released flux diminishes and after a period of about 1000–3000 h (for our experimental conditions) the flux remains at a constant level. The first period is due to the surface dissolution and to the diffusion of the main quantity dissolved in the pore solution at the initial time. The second period is governed by a stationary regime between the dissolution and the diffusion. The model coupling the transport and chemical phenomena in the pore solution, at the monolith surface and in the leachate gives satisfactory results for both mineral and organic species.

The experimental and modelling results show the influence of the leaching conditions on the organic pollutant behaviour and the main physico-chemical parameters responsible for the pollutant mobilisation: the solubility (enhanced by the co-solvent), the surface dissolution of the sample material at short term and the pore diffusion for long term leaching. The s/s organic pollution may be significantly released towards environment under certain leaching conditions. For a given leaching scenario the consideration of the dissolved organic matter in the leachate is unavoidable, its influence on the pollutant mobilisation has to be assessed experimentally and by modelling.

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