

Using PHREEQC for modelling and simulation of dynamic leaching tests and scenarios

L. Tiruta-Barna*

UMR5504, UMR792 Ingénierie des Systèmes Biologiques et des Procédés CNRS, INRA, F-31400 Toulouse, France

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Abstract

This paper presents an extension of the application field of PHREEQC geochemical software for modelling the dynamic leaching tests (and scenarios) by taking into account the leachant compartment as complex reactive/transport system and the coupling of many reactive compartments linked by substance fluxes.

This study focuses on the specific case of dynamic leaching of monolithic porous materials (particularly the case of continuous monolithic leaching test, CMLT) where reaction/diffusion occurs in the porous matrix and where the leachant is a complex reactor in which chemistry coupled with inter-phase mass transfer and convection processes take place.

It is demonstrated here that the modelling of open reactors (convection) is possible with PHREEQC by using RATES and KINETICS keyword data blocks. The PHREEQC model was validated by results comparison with analytical solutions of the system equations.

Coupling a diffusion compartment with an open reactor (complex boundary conditions for the diffusion equation) requires the introduction of a stagnant cell on the first grid cell of the diffusion compartment in TRANSPORT data block and the use of MIX function for model the monolith/leachant interface transfer. The proposed model was validated by comparison with numerical solutions obtained with MATLAB and by a numerical sensibility study.

Finally, the model equations are given for a complex dynamic leaching process of a porous monolith involving beside reaction/diffusion in the monolith, reactions, interface mass transfers, gas absorption and convection in the leachant. Examples of PHREEQC modelling are presented: (1) the case of continuous leaching of a cement based material using carbonated water and (2) a field scale water storage pool constructed with a solidified/stabilised material. The comparison with the experimental leaching data shows the simulation results are very satisfying.

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1. Introduction

The assessment of the environmental performances of various materials placed in real scenarios implying contact with water is a topical activity for industrials, scientifics and stake holders because of the risk of pollutant release by leaching and generation of significant environmental burdens. Among the categories of scenarios and materials undergoing leaching processes are the construction materials during their service life, recycled wastes in construction, landfilled wastes or waste heap stocking.

Environmental assessment of waste and material storage or use scenarios involving contact with water requires knowledge concerning material/water contact conditions and their influence on potential release of pollutants from such materials. Such information may be obtained from appropriate leaching experiences at laboratory, pilot or field scales and behavioural models, which should allow the identification of the main chemical and mass transfer mechanisms and the competition between different dynamic processes and their relative importance over a given time scale. In the case of mineral wastes (or containing low amounts of organic mater), the assessment tools at laboratory scale are leaching tests, some of them being regulatory at national or European levels.

The main differences between the various real environmental scenarios and also between the different leaching tests are due to the solid/liquid contact conditions, material granulometry, stir-

* Correspondence address: INSA Toulouse, LISBP, 135 av de Rangueil, F-31077 Toulouse cedex 4, France. Tel.: +33 5 61 55 97 88; fax: +33 5 61 55 97 60.

E-mail address: Ligia.barna@insa-toulouse.fr.

ring and liquid circulation. The specific leaching behaviour of a given material depends on the chemical nature of the material and its morphology, on the leachant composition and on the specific solid/liquid contact conditions, i.e. mass transfer properties.

This study focuses on the specific case of monolithic porous materials immersed in a leachant where the dynamic processes play an important role for the pollutant release. In porous matrix the diffusion is the main transport process while at the leachant level inter-phase mass transfer and convection can occur. In certain cases the leachant is stagnant, or renewed periodically, or renewed in a continuous flow.

Leaching behaviour interpretation and modelling requires taking into account of different transport and chemical phenomena with different complexity levels. In most cases the chemistry is very complex because of the chemical nature of the studied materials and high-performance numerical tools coupled with huge thermodynamic data bases are needed. Such modelling tools for the aqueous chemistry are well known as geochemical software and some of them are used for decades (e.g. MINTEQA2, EQ3/6, WATEQ4F, Geochemist's workbench, CHESS, PHREEQC). Softwares coupling geochemistry and transport are more fewer and they are more specific for geohydrology problems (like HYTEC, PHAST). Their use requires specific competence on numerical modelling making them not easy to use for everyone interested on material leaching problematics.

The modelling of leaching phenomena in the case of a porous monolith in contact with a leachate knows several steps of development briefly described below.

1) The modelling of the diffusion in the porous system of the monolith coupled with several chemical interactions was developed since more than a decade. These kinds of models do not consider the leachate as a physical compartment in which reactions and transport processes occur. The chemical model is almost always limited at several species and precipitation reactions. The examples encountered in the literature concern the leaching of cement based monolithic materials in a sequential dynamic leaching test [1–3].

More recently, the diffusion coupled with chemical reactions in the porous system was modelled using general chemical speciation models and codes coupled with solvers for the diffusion equation. Among these numerical models, which nevertheless still remain of limited spread, we cite SBLEM code developed by Park and Batchelor [4] or ORCHESTRA code developed by Meeussen [5] (examples of application are given in ref. [6]).

2) Literature examples of modelling of diffusion processes coupled with an external mass transport of the leachate and chemical reaction in the material compartment and in the leachate are scarce. These coupled chemical/transport models are ad hoc developed for particular cases and resolved by authors' own softwares [7–9]. The most important limitation of these models is the chemical part which takes into account only a small number of reactions and species.

3) Very recently high-performance softwares were applied to model complex chemistry coupled with diffusion in mono-

lith materials and with an external reactive transport process (flow and chemistry of leachate). Thus, PHREEQC [10] was used for modelling the laboratory leaching test and for simulation of a leaching scenario—a bloc immersed in a water flow [11]. HYTEC, a coupled geochemical/transport software for geohydrology [12], was used for modelling a monolith leaching test with continuous flow of the leachate [13].

Among the geochemical softwares PHREEQC presents the advantage to couple the full geochemical model with certain transport phenomena, allowing to simulate percolation (with a constant flow) or diffusion in some simple systems while keeping the numerical performances. One adds at these capabilities the compatibility with several data bases and the advantage to be an open source and easy to use. PHREEQC knows a real success being more and more used to model the leaching processes implying mineral wastes, soils and construction materials. Nevertheless the transport model is limited to very simple systems. Except the case of percolation column, only a closed batch reactor is considered where equilibrium or kinetic reactions occur without transport phenomena.

The objective of this paper is to present an extension of the application field of PHREEQC notably for the dynamic leaching tests and scenarios modelling taking into account the leachant compartment as complex reactive/transport system.

2. Dynamic leaching tests and scenarios

The dynamic leaching test of concern is particularly the monolithic leaching test with continuous renewal of leachate (CMLT), this test being under regulation in Europe.

The principle of the test is the leaching of a block of about 65 cm^3 (generally cubic or cylindrical) immersed in a constant volume of leachant renewed with a constant flow rate. The usual liquid volume/solid surface ratio is of $10 \text{ cm}^3/\text{cm}^2$ but other values are also used (2, 8, etc.). The leachant is generally pure water but can also be a chemical solution and/or be in contact with a gas phase. The classical tank leaching test (TLT) with sequential leachant renewal at different time intervals represents a particular case of the CMLT when the flow rate is zero. The principles exposed here can also be extended for the compacted granular leach test (CGLT).

The same physico-chemical processes are encountered at field scale in real leaching scenarios involving different exposure and leaching conditions, as for example: (i) immersion in underground or surface water of foundations, dykes, storage or quarry filling scenario; (ii) surface run-off of water (rain) on construction materials or landfill stabilized waste, etc.

Fig. 1 shows a simplified scheme of the mechanisms involved in the leaching process. When the material is immersed in water, the dissolution/precipitation processes begin at the solid/pore-water interface together with chemical reactions (acid/base, complexation, redox) in the aqueous phase. At the same time, the different soluble chemical species diffuse through the pores from the core to the surface of the material and are found in

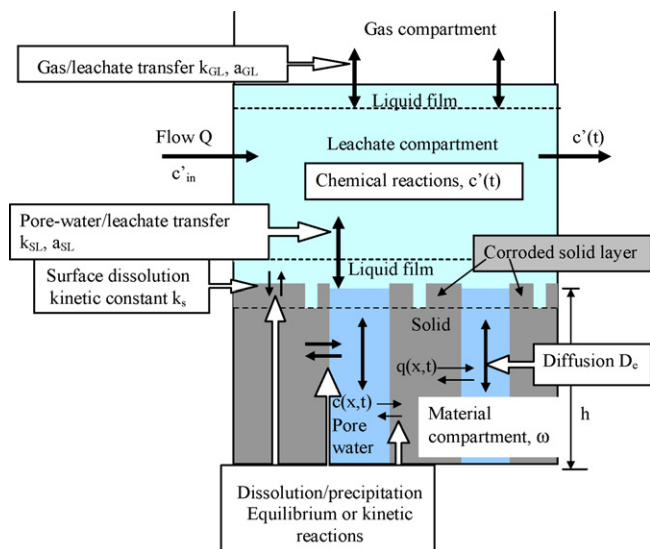


Fig. 1. Scheme of the modelled system and main physical and chemical mechanisms involved in the leaching processes.

the leachate. The changes in pore-water composition due to diffusion affect the solubility of the solid phases.

The surface of the block is in contact with the leachant which represents an aggressive solution because its composition is generally very different from that of the pore-water. Therefore a dissolution process may also occur at the leachant/block contact surface (the surface corrosion).

The leachate composition is determined by the mass flows from the pores (diffusion), the surface dissolution of the material, the chemical reactions, the interactions with a gas phase and by the leachant flow and hydrodynamics.

The leaching model must consider: (1) chemical reactions and transport mechanisms in the porous system of the material and (2) chemical reactions and transport processes in the leachant. The two compartments, material and leachate, exchange fluxes of chemical species. Before the presentation of the leaching model for the system schematised in Fig. 1, the implementation in PHREEQC of main transport processes will be described here below.

3. Modelling of open stirred reactors with PHREEQC

The conceptual coupled chemical/transport model implemented in PHREEQC is explained elsewhere [10] only the main principles are remembered here. The chemical speciation at equilibrium is defined by a set of equations representing the mass balance law (equilibrium constants) for each chemical element and the electrical charge balance. The set of equilibrium equations is resolved by the Newton–Raphson algorithm and the result is the concentration of each chemical species in each phase including the pH and the pe.

PHREEQC has the capability to simulate some dynamic processes like: reaction kinetics (introduced by the keywords RATES and KINETICS), 1D liquid flow with plug flow hydrodynamic (keyword ADVECTION) or advection–dispersion hydrodynamics with stagnant zones (keyword TRANSPORT).

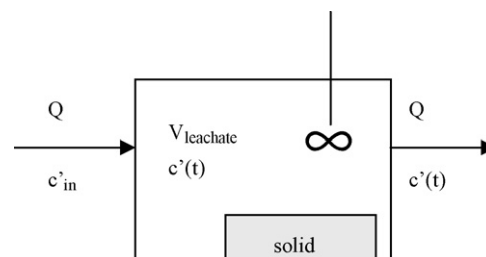


Fig. 2. Principles of an open stirred reactor.

The integration of kinetic equations over time is realised by a Runge-Kutta algorithm. The partial differential equations describing the transport processes are resolved by an explicit finite difference algorithm. In order to calculate both equilibrium and dynamic processes a split-operator scheme is used. At each time step (the time grid is calculated following numerical stability and dispersion criteria) the kinetic and equilibrium reactions are calculated after the advection and dispersion step. In the following we only consider the dynamic aspects of the coupled reaction/transport model, the equilibrium reactions model being unchanged and representing the core of PHREEQC.

At laboratory scale the stirred open reactor is very often used as experimental device and operational mode. In leaching tests as CMLT or CGLT, as well as in many real leaching scenarios the leachate compartment behaves according to the open stirred reactor scheme (Fig. 2). PHREEQC has not a dedicated module to simulate the open stirred reactor. Supposing an element existing as soluble and solid species in the open stirred reactor, the evolution in time of its total concentration is determined by the leachate hydrodynamics and by all kinetic reactions. The time depending mass balance equation is composed of a convection term and of the sum of kinetic terms:

$$\frac{dc'}{dt} = \underbrace{\frac{Q}{V_{\text{leachate}}}(c'_{\text{in}} - c')}_{\text{convection}} + \underbrace{\sum v_k R_k}_{\text{reaction kinetics}} \quad (1)$$

where c' is the concentration of an element in soluble forms, c'_{in} the concentration at the reactor inlet, V_{leachate} is the volume of the reactor filled with the liquid phase, Q is the flow rate (considered constant). R is the k th reaction rate and v is the stoichiometric coefficient in this reaction. Eq. (1) is written for all chemical elements. A set of equations are added to the Eq. (1) in order to calculate the equilibrium speciation in the system as explained at the beginning of these paragraphs.

In PHREEQC the explicit mathematical expression of reaction rates can be introduced by the user in RATES keyword data block in Basic program language. The specific parameters values, including the species name and stoichiometric coefficient, are defined in KINETICS keyword data block. Each reaction kinetic is defined individually the variable calculated in RATES being the variation of mole number of a given species for a time interval.

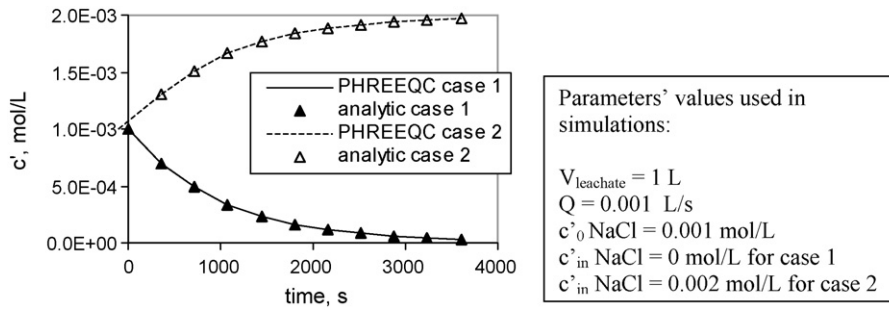


Fig. 3. Na^+ concentration in the leachate for: case 1—pure water at the reactor inlet; case 2— Na^+ solution at the reactor inlet.

The idea developed here is to add the convection term as a “reaction kinetics” defined in RATES data block:

$$\Delta c' = \Delta t \left(\frac{Q}{V_{\text{leachate}}} (c'_{\text{in}} - c') \right) \quad (2)$$

As the convection flow concerns all elements existing in the liquid phase (except H and O while the reactor volume and thus water mass is constant) the mass balance equation and thus the convection term must be written for all these elements.

A very simple example considers an open stirred reactor containing c'_0 mol NaCl dissolved in 1 kg water. For the case 1 pure water enters the reactor and the leachate flows out with a constant flow rate Q . The objective is to calculate the concentrations of elements Na and Cl in the leachate versus time. The case 2 shows the concentration evolution when a solution of NaCl enters the reactor with c'_{in} (the parameters' values are given in Fig. 3). The PHREEQC program for this example contains a SOLUTION data block where Na and Cl are set to $c'_0 = 0.001$ mol/L (or kg water), a RATES and KINETICS blocks the details are given in Fig. 4.

The PHREEQC result is compared in Fig. 3 (only Na concentration is represented) with the analytical solution for case 1:

$$c' = c'_0 \exp \left(-\frac{t Q}{V_{\text{leachate}}} \right) \quad (3)$$

and the analytical solution for case 2:

$$c' - c'_{\text{in}} = (c'_0 - c'_{\text{in}}) \exp \left(-\frac{t Q}{V_{\text{leachate}}} \right) \quad (4)$$

The calculation was done for 3600 s with 10 results shown at 3600/10 s intervals. In the program listing TIME is the name of the integration time step (Δt) and is calculated by the Runge-Kutta algorithm (in this example a default 3rd order Runge-Kutta is used; for more details see the PHREEQC guide).

No differences are observed between the two results – analytical solution and PHREEQC solution – that validates the PHREEQC model.

4. Coupling a diffusion compartment with an open stirred reactor

The scheme of a porous block (diffusion compartment) in contact with a leachate (open stirred reactor) is presented in Fig. 5a. For a given chemical element of concentration c the balance equation taking into account 1D diffusion in pore-water is:

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} - \sum \frac{\partial q}{\partial t} \quad (5)$$

with

$$D_e = f(\tau)D \quad (6)$$

D is the molecular diffusion coefficient in water and $f(\tau)$ a tortuosity function. D_e is named by some authors effective diffusion coefficient and by other apparent diffusion coefficient. We adopt here the nomenclature used in PHREEQC, i.e. effective diffusion coefficient. The second term represents the source/sink term due to all dissolution/precipitation reactions implying the con-

```

RATES
  FLOW_Na
  -start
  10 totalelement = TOT("Na")
  20 IF(totalelement <= 0) THEN GOTO 60
  30 rate = parm(1)/parm(2)*(parm(3)-totalelement)
  40 moles = rate*TIME
  50 IF(totalelement+moles < 0) THEN moles = -totalelement
  60 SAVE moles
  -end
KINETICS 1
FLOW_Na
  -formula Na+ 1
  -m 1
  -m0 1
  -parms 0.001 1 0
  -tol 1e-008
  -steps 3600 in 10 steps # seconds
  -step_divide 1
  -runge_kutta 3

```

In the program:

- parm(1) = Q
- parm(2) = V_{leachate}
- parm(3) = c'_{in} (equation 2)

Fig. 4. Fragment of the PHREEQC program for simulation of an open stirred reactor.

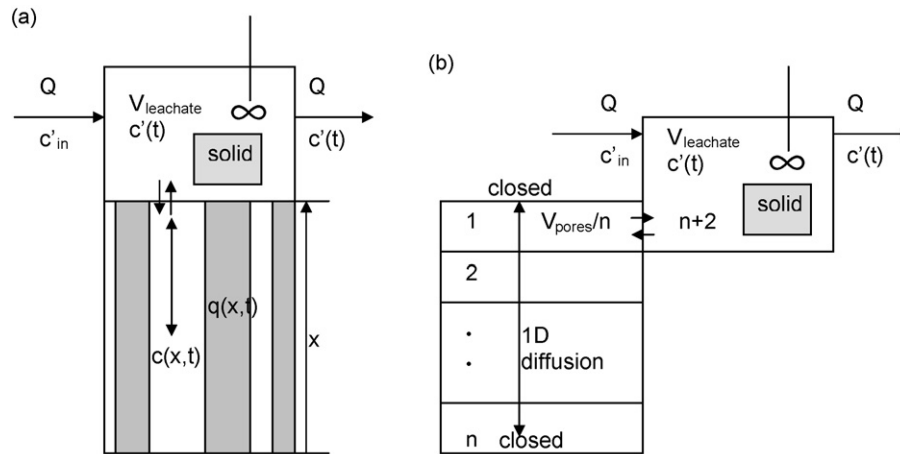


Fig. 5. (a) Scheme of the diffusion compartment coupled with an open stirred reactor. (b) PHREEQC model.

sidered chemical element; q is the concentration of a solid phase (mol/L) involved in a kinetic reaction.

The boundary conditions are:

- at the bottom face ($x=0$):

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = 0 \quad (7)$$

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

$$\omega D_e \left. \frac{\partial c}{\partial x} \right|_{x=h} = k_{SL}(c' - c|_{x=h}) \quad (8)$$

where $c|_{x=h}$ is the concentration in the diffusion compartment at the leachate interface, ω is the open porosity, k_{SL} (m/s) is the mass transfer coefficient between the leachate and the pore-water at the surface of the block (in the hypothesis of linear driving force transfer). The specific solid/liquid exchange surface a_{SL} (m^2/m^3) is defined by:

$$a_{SL} = \frac{A_{block}}{V_{leachant}} \quad (9)$$

Eq. (8) expresses the diffusion flux transferred towards the leachate. It appears also in the balance equation for the liquid phase of the open stirred reactor (the first term named "diffusion" here below):

(10)

Modelling 1D diffusion with PHREEQC is possible using the keyword data block TRANSPORT. In the numerical grid scheme presented in Fig. 5b the cells are numbered as in PHREEQC algorithm. The boundary conditions implemented in PHREEQC are not compatible with the condition at the leachate/block interface given by Eq. (8) where c' is a function of time. More, the

leachate is a compartment with different chemical and physical properties requiring its own model.

A solution for the exposed problem is to use the stagnant_cells option in TRANSPORT. A "stagnant cell" is considered linked to the cell 1 of the grid as shown in Fig. 5b the properties of which can be defined independently by the data blocks SOLUTION, EQUILIBRIUM_PHASES, KINETICS, etc. The first cell of the grid is a "transfer" cell with all initial chemical parameters at 0 and without source/sink terms.

In real cases the mass transfer at the block/leachate interface is faster than the diffusion process which is in fact the limiting process. So the interface transfer can be considered very rapid ($a_{SL}k_{SL}$ high value) and even instantaneous that is equivalent to mixing the content of the two cells (1 and $n+2$). In this case the simplest method to link cell 1 and $n+2$ is to use MIX function.

To illustrate the application of the proposed model a simple example is presented below. One considers a porous block containing Na as soluble element in pore-water, the block being in contact with a leachate. The evolution of the leachate concentration in time is calculated with PHREEQC and with a numerical model resolved under MATLAB in order to compare the numerical results and validate the PHREEQC model. The resolution under MATLAB is based on a space grid of 100 meshes (value optimised after a parameter sensibility study) and on a MATLAB implemented ordinary differential equation solver for integration over time. Fig. 6 shows the simulation results using the parameters specified at right of the graph. Case 1 example corresponds to a closed reactor (no leachate flow) in which Na accumulates while case 2 corresponds to an open reactor in which pure water enters with a constant flow rate and the leachate leaves charged with Na at concentration $c'(t)$.

The PHREEQC program contains the following data blocks: SOLUTION for cells 2–100 with 0.1 mol/L Na, RATES and KINETICS for the flow contribution in cell 102, TRANSPORT for diffusion in cells 1–100 and MIX for "stagnant cell" 102 linked to cell 1. TRANSPORT and MIX blocks are given in Fig. 7. The value of a MIX parameter is the volume fraction of the respective cell, e.g. $MIX\ 1 = V_{cell1}/(V_{cell1} + V_{cell102})$.

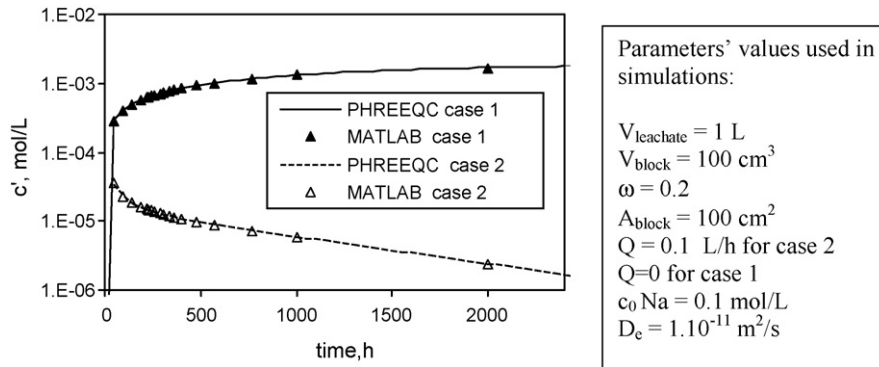


Fig. 6. Na^+ concentration in the leachate for: case 1—no flow; case 2—constant flow rate water.

The number of cells in TRANSPORT was chosen after a numerical sensibility study of the model and after comparison with analytical solutions or MATLAB numerical solutions. A number of 100 cells was sufficiently high in all simulation trials and was adopted for modelling different leaching examples.

5. Dynamic leaching model using PHREEQC

After resolving the problem of the leachate transport and interface mass transfer, the leaching model for the system depicted in Fig. 1 can be developed.

For the porous material block the mass balance equation (5) with boundary conditions (7) and (8) are written for each element. The one-dimensional diffusion equation is used as a good approximation by considering an equivalent sheet geometry (which is a model case for the one-dimensional diffusion) with the same material volume V_{block} (imposed by the block mass balance) and the same contact surface area A_{block} and exposed to leachate by only one face. The equivalent sheet is of thickness h :

$$h = \frac{V_{\text{block}}}{A_{\text{block}}} \quad (11)$$

```

TRANSPORT
-cells                100
-shifts              100
-time_step           180000 # seconds
-flow_direction      diffusion_only
-boundary_conditions closed closed
-lengths             100*0.0001
-diffusion_coefficient 1e-011
-stagnant            1 0 0 0
-print_cells         102
-punch_cells         102
-warnings            true

MIX 1
1      0.0002
102    0.9998

MIX 102
1      0.0002
102    0.9998
  
```

Fig. 7. Fragment of the PHREEQC program for coupling a diffusion compartment with an open stirred reactor.

In the leachate compartment the accumulation of an element is determined by the flux from the material, from transport due to convection, from dissolution/precipitation reactions of the solid phases containing the considered element and also from the surface corrosion. Uptake and reaction of gas species can also be considered. The time depending balance equation for each element (concentration c') in the leachate can then be written:

$$\frac{dc'}{dt} = - a_{\text{SL}} k_{\text{SL}} (c' - c'_{|x=h}) + \frac{Q}{V_{\text{leachate}}} (c'_{\text{in}} - c') - \sum v_k \frac{\partial q'_k}{\partial t} + a_{\text{GL}} F_{\text{abs}}$$

↓
diffusion

↓
convection

↓
pp/dis

↓
gas absorption

(12)

where q' are respectively the concentrations of solid phases in the leachate and on the corroded surface layer (involved in dissolution/precipitation reactions). F_{ab} is the gas absorption flux ($\text{mol}/(\text{m}^2 \text{ s})$) the equation depends on the specific absorption model chosen for each case [14]. The specific gas/liquid exchange surface a_{GL} (m^2/m^3) is defined by:

$$a_{\text{GL}} = \frac{A_{\text{leachate}}}{V_{\text{leachate}}} \quad (13)$$

This transport model has to be completed with the chemical model (the equilibrium and charge balance laws) resolving the speciation problem. The concentrations c and c' are the sums of concentrations of all soluble species of a given element respectively in the pore-water and in the leachate. Details of the model development and application examples in the case of leaching of monolith materials in different material/leachant contact conditions are given in refs. [7,9,11,15].

For this complex leaching system the core model in PHREEQC is composed of:

- TRANSPORT block with diffusion_only option and one stagnant cell (numbered 102),
- MIX for grid cell 1 and the stagnant cell 102, as described in paragraph 3, for taking into account the “diffusion” term in Eq. (12),
- RATES and KINETICS block for the leachant (the stagnant cell numbered 102) in which all the other dynamic processes and kinetic reactions composing the Eq. (12) are defined. The convection term is introduced as explained in paragraph 2 for

all chemical elements composing the geochemical model for each considered material and

- SOLUTION, EQUILIBRIUM_PHASES, SURFACE, etc. are defined if necessary following the chemical nature of the modelled system.

A first example of CMLT modelling in the case of a cement based solidified/stabilised material is presented here below. As described in the above cited references, the methodology for leaching behaviour assessment is based on equilibrium leaching tests (like the acid neutralisation capacity ANC test [16]) and dynamic leaching tests in different contact conditions (TLT, CMLT). The methodology can be structured in several steps: (1) a geochemical model of the material in contact with water is developed based on mineralogical data (or knowledge of the material) and on equilibrium leaching tests like ANC; (2) transport parameters are identified, i.e. diffusion coefficients are calculated using the results of simple dynamic leaching tests like TLT for nonreactive elements (e.g. Na, K); (3) the leaching behaviour in dynamic conditions is modelled using the whole experimental results obtained by the different tests. The methodology details and geochemical modelling approach are exposed elsewhere, e.g. in ref. [17].

For the example considered here (more details concerning the experimental work in refs. [11] and [18]) the concentration of main elements (Ca, Na, K, Si, Al, Mg) and pollutants (S, Ba, Cd, Cu, Mo, Pb, Zn) have been monitored in the leachates of all leaching tests performed (ANC, TLT, CMLT). A geochemical model was at first developed using PHREEQC with LLNL data base. The main solid phases for the major and pollutant elements were identified starting from XRD identifications and on their solubility measurements in leachate in function of the leachate pH (ANC test). Phases like: hydrated calcium-silicates (CSH), albite, barite, brucite, calcite, gypsum, magnesite, ettrin-

gite, $\text{Cd}(\text{OH})_2$, $\text{Cu}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ were considered to be very likely to occur in the material or to form at the material/water contact.

The main transport parameter in this example is the effective diffusion coefficient. It was determined by fitting the transport model for soluble nonreactive species (Na^+ , K^+) using the experimental results of a dynamic leaching test with periodical renewal of the leachate (TLT).

The CMLT trials were performed using carbonated water as leachant. The test duration is divided in three intervals as follows: in the first and second intervals during respectively 0.2 and 2 days the leachant is stagnant ($Q=0$) and totally renewed at the end of each interval; for the rest of the test duration of about 60 days the leachant containing a constant CO_2 concentration is continuously renewed with a constant flow rate. The concentration of major and pollutant elements and the leachate pH have been monitored in time and served as control data for the simulation results.

The PHREEQC model of the CMLT is composed of three successive simulations corresponding to the three time intervals in which the experimental conditions are different. For each simulation the program contains the subsystem models developed in the two previous paragraphs.

As Fig. 8 shows the simulation concentrations and the experimental concentrations are of the same order of magnitude which is rather a good result for a geochemical modelling. In certain cases the concentrations measured in the leachates are below or very close to the detection limit introducing an unevaluated uncertainty for the comparison. A good agreement is also observed for the pH.

The second example concerns a pilot scale leaching scenario. A water storage pool of a capacity of about 20 m^3 is constructed with a solidified/stabilised material containing a mineral waste and a hydraulic binder.

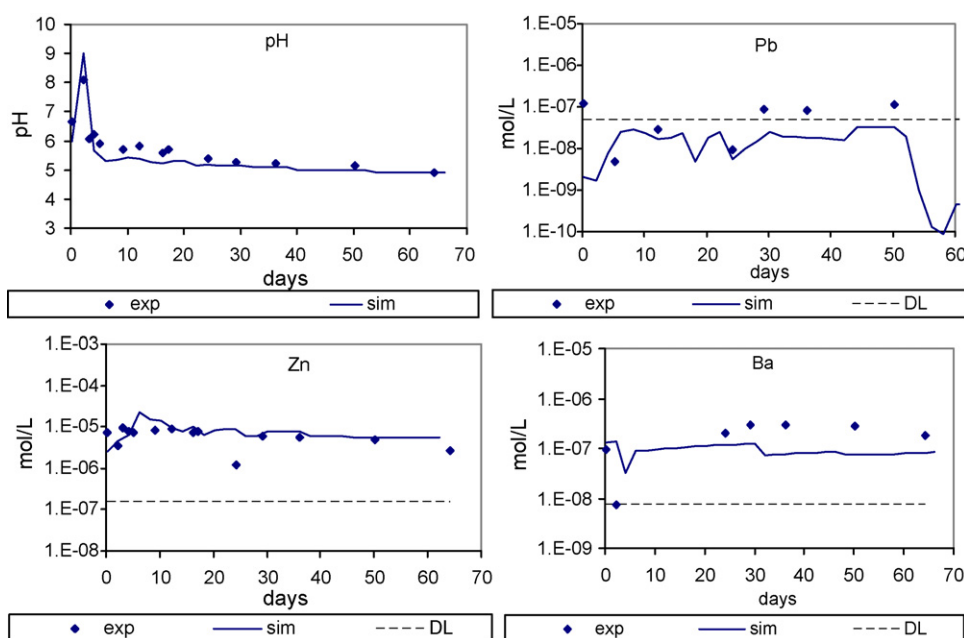


Fig. 8. Leaching with carbonated water. Experimental (exp) and simulation (sim) results (DL = detection limit).

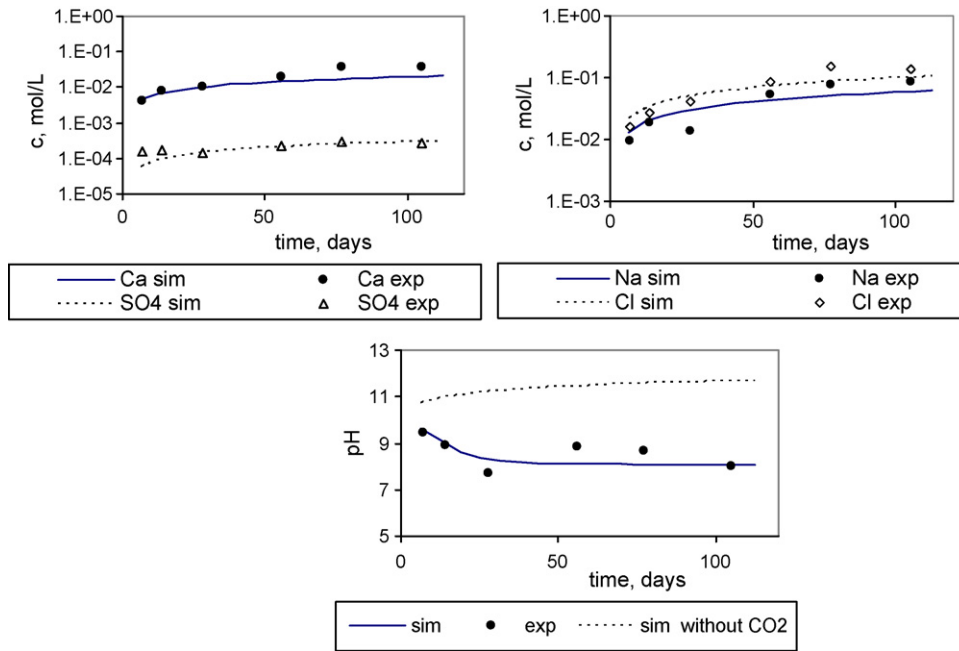


Fig. 9. Leaching in a real scenario. Experimental (exp) and simulation (sim) results.

The stored water (named here the leachate) was in permanent contact with the construction material and with the atmosphere, without renewal of the liquid for about 100 days. During this period the composition of the pool has been monitored and significant concentration in alkaline elements, Ca, Cl and SO₄ have been measured as well as an alkaline pH of about 9. Concerning the material composition, an important content on soluble Na, K and Cl has been determined by the mean of ANC test and a basic character of the material has been observed in agreement with its high content in portlandite (details on material composition and properties in ref. [19]). The detailed characteristics of the pilot have been presented in a previous work [7]. The leaching model considered the main physico-chemical mechanisms in the material and leachate compartments. During the water storage the soluble elements diffuse from the pore-water and CO₂ is uptaken because of the basic character of the liquid. Carbonation of the leachate and of the material is then expected.

The experimental data were reused here with the aim to exemplify the application of the PHREEQC leaching model. The model parameters, i.e. geometrical characteristics, chemical composition of the material, mean diffusion coefficient, are the same as those defined in ref. [7]. A simple geochemical model is considered in which alkaline elements and Cl are at soluble state in the pore-water and phases like portlandite and gypsum are considered responsible for Ca and SO₄ release at least for short and mean leaching time. Here the leachate compartment is no flowing ($Q=0$) but open for dynamic exchanges with the atmosphere. For CO₂ absorption and reaction in the leachate ($\text{CO}_{2(\text{aq})} + \text{OH}^- = \text{HCO}_3^-$) the reaction kinetics depends on the pH domain as exposed in ref. [14]. A rapid reaction rate is expected to be used in Eq. (12) defined by:

$$F_{\text{ab}} = k_{\text{GL}} \left(\frac{p_{\text{CO}_2}}{K_{\text{H}}} - c'_{\text{CO}_2(\text{aq})} \right) \quad (14)$$

where p_{CO_2} is the CO₂ pressure in normal atmosphere, K_{H} is the Henry's constant for CO₂ and k_{GL} (m/s) is the mass transfer parameter depending on the CO₂ reaction rate and CO₂ diffusion coefficient in water.

The PHREEQC model is composed of a TRANSPORT block with one stagnant zone and MIX functions for modelling the diffusion flux towards leachate, RATES and KINETICS for the leachant compartment for CO₂ dynamic uptake, SOLUTION and EQUILIBRIUM _PHASES for chemistry definition in pore-water and leachate. The simulation results presented in Fig. 9 are of the same order of magnitude as the experimental data and show a good agreement with the measured concentrations. The model describes the pH evolution in time and the important effect of atmospheric CO₂ uptake: for comparison the figure shows the leachate pH calculated in the case of absence of CO₂. In the model Na⁺ and Cl⁻ are considered as nonreactive elements their release being governed by the transport processes. Or the simulation curves do not describe very well their behaviour. This aspect can be explained by an evolution of the porous matrix like an increase of the porosity with the leaching time. It should be also mentioned that the experimental data are obtained by sampling on the field pilot and that no replicates are available.

6. Conclusions

The actual capabilities of PHREEQC are limited from the point of view of mass transfer processes. Often the experimental protocols designed to investigate the complex solid/liquid/gas reactions involve specific inter-phase contact conditions and fluid circulation. The open stirred reactor is a basic experimental device very often used in such specific studies as for example the various leaching tests.

It is demonstrated in this work that it is possible to model an open stirred reactor in PHREEQC by using RATES and KINET-

ICS data blocks. This model is based on the similarities between the formalism of the reaction kinetics and the formalism of the mass balance of an open stirred reactor. Nevertheless more complicated reactor hydrodynamics (like non-ideally stirred reactors) implying a spatial distribution of concentrations cannot be modelled by this way.

The second modelling aspect is the consideration of diffusion process in a system with complex boundary conditions when the diffusion flux at the block/leachant interface depends on the leachate composition. This mass transfer case can be modelled by considering a stagnant cell in TRANSPORT block with MIX function for a rapid transfer. Here the “stagnant cell” represents the leachant which can be an open (or closed) stirred reactor (“stagnant cell” is only the PHREEQC terminology; this does not mean that the leachant is really a stagnant fluid).

With the here proposed solutions for the two transport problems, a lot of leaching tests and scenarios can be modelled using PHREEQC. The more complex situation is the case of a porous reactive monolith immersed in a flowing leachant in which complex chemical reactions and mass transfer processes occur. The time dependent mass balance of an element in the leachant compartment is composed of many time dependent terms like: (i) kinetic reactions, (ii) diffusion flux towards leachate, (iii) transport by convection with the liquid flow, (iv) multi-inter-phase transfer processes (like liquid/gas transfers). The examples given in this paper (a leaching test and a field pilot) demonstrate the feasibility of such complex modelling cases by using PHREEQC.

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