

Assessment of the multi-scale leaching behaviour of compacted coal fly ash

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Abstract

Peer experimental–modelling tools were developed and applied in the case of coal fly ashes with the aim to assess the leaching behaviour of ash compacted layers in a use scenario. Laboratory-scale (dissolution kinetics, ANC test, column percolation) and field pilot experimental studies (release monitoring during 18 month, hydrodynamic study, ANC on 44 month leached waste) were performed in order to identify and quantify the main transport phenomena and chemical processes.

A quantitative geochemical model was developed taking into account equilibrium chemical reactions as well as kinetic processes for silicate phases like albite, K-feldspar and Ca-olivine. Phases like $Ba_xSr_{1-x}(SO_4)_y(CrO_4)_{1-y}$ were proposed to explain the complex leaching behaviour of As, Cr, Ba, S; the soluble $CaMoO_4$ seems to control the Mo concentration. At neutral and acid pH, the model of surface complexation on ferric hydroxides was added for describing the behaviour of As, Cr, and Mo.

At each scale the dynamic processes were identified and quantified by modelling. During the first contact with water an equilibration time of about 10 days was identified and then considered in all other laboratory experiments (ANC, column percolation). The hydrodynamic properties of compacted fly ashes were identified: a high water retention capacity (97% of the pores are still filled after draining under normal pressure), a flow regime close to plug type, a low fraction of stagnant zones (<0.03%). The scenario factors like carbonation and rainfall play an important role on the leaching behaviour at field scale. The carbonation diminishes the leachate pH from 11 to 8.5. The alternation of rain periods determines an apparent batch behaviour which slows down the outflow of the initial soluble fraction in pore water, if compared with the laboratory percolation column.

The coupled geochemical–transport model was validated by comparison of the simulation results on ANC data obtained on the waste after 44 months of leaching under natural conditions.

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1. Introduction

Thermal process residues such as coal fly ashes are produced world-wide in ever increasing quantities. They are a potentially marketable secondary material [1], which can be reused for example in road construction. However, giving the waste chemical composition, this use may cause environmental impacts over the lifetime of the work, particularly could adversely affect the groundwater quality. No studies are known related to the envi-

ronmental risk or impacts complete assessment for such reuse scenarios [1]. The main challenge of environmental studies of residues is the prediction of pollutant long-term release usually described by a leaching model. To develop such model, extensive leaching programs in laboratory followed by field site verification are decisive. It is also accepted that the behaviour of a material depends on its intrinsic physico-chemical properties but also on external factors, specific to the scenario of use or storage. A methodology, the European standard ENV 12920 [2], was developed in order to characterise the behaviour of wastes-materials in such scenarios. This methodology is centred on laboratory tests and behavioural models describing the pollutant release. One of the major problems in the application

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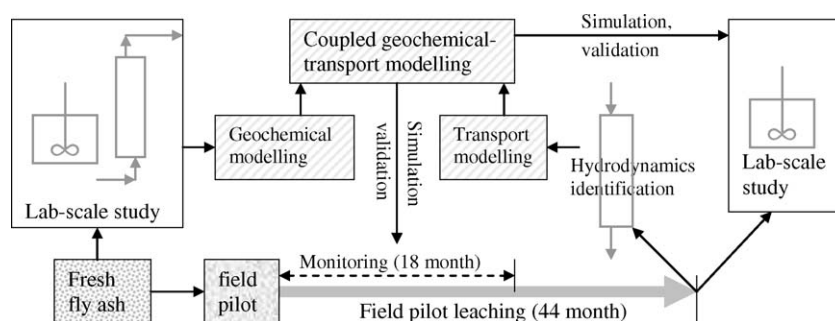


Fig. 1. Conceptual scheme of the study methodology.

of different experimental and modelling tools is the time scale and space scale extrapolation, in other words the consideration of the appropriate physico-chemical phenomena at different levels in order to accurately interpret the experimental data and/or to develop high-performance models. In the case of mineral wastes, the experimental tools mostly used with ENV12920 are laboratory leaching tests as acid neutralisation capacity (ANC), percolation in saturated column, monolith leaching, etc. The duration of all current laboratory tests varies from 48 h [3] to 2 or 3 months and the solid/liquid system is considered governed by instantaneous chemical reactions, hypothesis implying erroneous interpretation of test data. In the case of evolving systems like those characterised by slow reactions (typically solid/liquid systems), the experimental results have to be carefully interpreted and the extrapolation to longer periods requires knowledge about the material weathering dynamics. Other dynamic factors involved in the leaching process are the mass transport phenomena, i.e. diffusion and convective transport. The convective transport depends on the laboratory apparatus and experimental protocol used as well as on the scenario factors and parameters (granular material compaction, porous system, work geometry, water flow direction and local velocity, flow discontinuities, etc.). The convection process flushes out matter from the system and influences the reaction paths in an evolving chemical context as well as the mass transfers at solid/liquid interfaces. As a consequence, the transport phenomena have to be characterised and taken into account in the leaching model at each level and for each application case, simple extrapolation from a case or scale to another being not obvious.

The objectives of this paper are: (1) to propose a study methodology and to develop peer experimental–modelling tools and apply in the case of compacted coal fly ashes; (2) to quantify the different chemical and transport processes at different space and time scales; (3) to identify those of the mechanisms controlling the pollutant release in a real scenario.

The methodology designed and applied in this study is based on laboratory and field experiments and on modelling, as the Fig. 1 shows. Laboratory leaching tests (dissolution kinetics, ANC, column percolation) were performed on fresh fly ash in order to identify the chemical reactions and the reaction kinetics in the fly ash–water system, to develop a mineralogical model and to identify the main transport mechanisms. A coupled geochemical–transport model was developed on the basis of lab-scale experimental results. A large-scale demon-

stration site (lysimeter of compacted fly ashes) has been constructed and monitored for chemical element release during 18 months. Additional hydrodynamic studies allowed the characterisation of the transport processes on field and to adapt the geochemical–transport leaching model at field scale. ANC test was also performed on field samples after 44 months of leaching under natural conditions and the results were used for comparison and validation of the geochemical–transport model.

2. Materials and methods

2.1. Waste characterisation

A fresh, pulverised fly ash collected from a French coal fired power plant was used in this study. X-ray diffraction analysis was performed to obtain information on the bulk mineralogical composition. The total concentration of elements in the waste was determined by acid mineralization ($\text{HNO}_3 + \text{HCl}$) of the samples and analysis of eluates.

2.2. Analytical methods

After filtration the eluates were acidified at pH 2 with HNO_3 solution (65%) and then analysed for cations by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Jobin Yvon Ultima 2). Anions like SO_4^{2-} , Cl^- , Br^- were analysed by ion-chromatography (Dionex IC25). The standard deviation of analytical results expressed as concentrations is less than 5%.

2.3. Leaching behaviour assessment

2.3.1. Dissolution kinetics

The evolution of the solid–liquid system for short periods was assessed by a kinetic experimental study. Several samples containing quantities of ash and water corresponding to two L/S values (1 and 10) were stirred in closed polyethylene flasks, at room temperature. The liquid phases were analysed after filtration on $0.45 \mu\text{m}$ membrane filter at different times up to 60 days.

2.3.2. ANC test

The acid neutralisation capacity test was based on the methodology of the European standard prEN14429 [3]. It was carried out by mixing 150 mL of water containing various

amounts of HNO_3 with 15 g of ash in order to obtain a series of 6 batches with pH values ranging from natural pH to about 4. After equilibration and stirring for 10 days (equilibration time determined in the kinetic study) at room temperature, the solid residue was separated by filtration using a membrane filter of $0.45 \mu\text{m}$. The pH and the concentrations of the leached components in the eluates were measured.

2.3.3. CGLT test

The compact granular leaching test was performed in order to determine the diffusion coefficient in a compacted layer of fly ash, in the absence of a convective water flow. The assay was inspired from the Dutch standard NVN-7347 [4]. The fly ash was compacted in a polyethylene batch by tamping successive layers with a rammer in order to obtain a homogenous porosity. The liquid/surface ratio was maintained at $10 \text{ cm}^3/\text{cm}^2$ and the leaching solution renewal (demineralised water) was performed at 6 h, 18 h, 1, 2, 5, 7, 20 and 28 days. The concentrations of soluble elements, i.e. Na^+ and K^+ , were used to estimate the diffusion coefficient in the porous system by modelling.

2.3.4. Column assays

The column test was based on the methodology of characterisation of leaching behaviour (percolation test) known as European standard prEN14405 [5]. A 40 cm height and 9.4 cm diameter column was used. It was equipped with filters at the inlet and outlet. A quantity of 3.2 kg of moistened ash (16% humidity) was added to column in layers of a few cm and packed up to a height of 30 cm, resulting in dry bulk density of 1.29 g/mL . The column was first saturated with demineralised water and kept for 10 days to equilibrate the system. The water accessible pore volume V_0 was determined by the weight differences between the dry column and the water-saturated column. The corresponding porosity was $\varepsilon = 0.32$. When equilibrium was assumed to be reached in the column, demineralised water was passed upwards through the compacted ash at 0.7 mL/min . The leachate containing eluted constituents, generated during 60 days (corresponding to $L/S = 20 \text{ mL/g}$), was periodically analysed for the pH and the species concentrations.

At the end of the leaching experiments, the hydrodynamic parameters of the column were determined by tracer experiments using a 40 mmol/L LiBr solution. LiBr was chosen for the tracer experiment because Li and Br were not detected in the initial fly ash. In addition Br^- was assumed to behave like a chemical inert tracer (no reaction with the solid matrix). A volume of $2V_0$ of LiBr solution was passed through the column followed by distilled water ($Q = 5.11 \text{ mL/min}$) until total elution of Br^- . The outlet Br^- concentration versus time was used to model the column hydrodynamic behaviour.

2.4. Field pilot

2.4.1. Pollutant release

A lysimeter which simulates a coal fly ash embankment was constructed on the EEDEMS platform (www.eedems.com) with the aim to measure the pollutant flows generated by ashes under real natural exposure conditions. The lysimeter measured 40 m^2

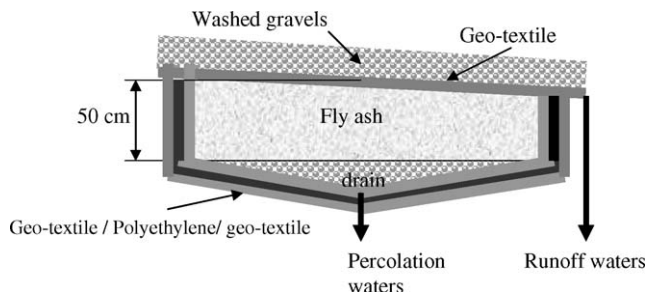


Fig. 2. Field pilot scheme.

of surface and 50 cm of height (Fig. 2). A polyethylene film sandwiched between two geo-textiles protective against punching was posed underneath and covered also the lateral sides of the lysimeter. A drain (11 cm diameter) was laid out on the longitudinal axis and covered with 20 cm of washed gravels for drainage layer. A rammer was used to tamped ashes in two layers of 25 cm height; the apparent density of the compacted ash was estimated at 1.2. The lysimeter upper surface was covered with a geo-textile maintained with a washed gravels layer. The lysimeter surface was tilted 5% for leading the runoff waters to a collecting gutter. The percolation waters (discharged via drains and discharge pipe) and runoff waters were collected in polyethylene barrels whose contents periodically was measured and sampled for analysis during 18 months.

2.4.2. Hydrodynamic study

After 44 months the pilot was dismantled. In order to understand the water movement in the compacted fly ash layer a hydrodynamic study was performed in laboratory on a carrot taken from the site. A steel cylinder of 20 cm of diameter and 60 cm high was used to take a sample over the whole thickness of the compacted ash layer (50 cm height). The experimental set-up used for the hydrodynamic study of this pilot column was the same as for the laboratory percolation column. An injection device was placed at the top of the cylinder in order to uniformly distribute the water in drops over the whole inlet surface and to simulate the rain. Artificial rain periods on alternate with dry periods were scheduled and the outlet flows were monitored in time. In the case of water sheet accumulated at the top of the pilot column the outlet flow was maximal and equal to 1.2 mL/min . More, in the case of stationary water flows, LiBr tracer was injected in the rain water in order to estimate the hydrodynamic dispersion in the pilot column.

2.4.3. ANC test applied to field leached waste

Samples taken from the site at 44 months were submitted to ANC test following the same protocol described in Section 2.3.2.

3. Modelling approach and principles

The main phenomena involved in the leaching process are the chemical reactions and the transport processes, i.e. diffusion and convection–dispersion. The identification of their nature and the quantification of these processes require a modelling step.

Each experimental assay performed in this study brought specific information about the species release mechanism and was treated by an appropriate modelling.

3.1. Diffusion coefficient determination

The one-dimensional diffusion equation with the boundary conditions below was applied to describe the ion transport in the porous system of the compacted fly ash:

$$\frac{\partial c}{\partial t} = D_a \frac{\partial^2 c}{\partial x^2}; \quad \frac{\partial c}{\partial x} \Big|_{x=0} = 0;$$

$$\varepsilon D_a \frac{\partial c}{\partial x} \Big|_{x=h} = k_{SL}(c' - c|_{x=h}) \quad (1)$$

where c is the concentration in the pore water, c' the concentration in the leachate, x the spatial coordinate, t the time coordinate, D_a the apparent diffusion coefficient, ε the porosity, k_{SL} is the mass transfer coefficient between the eluate and the pore water at the surface of the compacted layer. The balance equation of a given element in the leachate is given by:

$$\frac{dc'}{dt} = -\frac{1-E}{E} a_s k_{SL}(c' - c|_{x=h});$$

$$E = \frac{V_{leachate}}{V_{leachate} + V_{compacted\ material}}; \quad a_s = \frac{A_{compacted\ material}}{V_{leachate}} \quad (2)$$

a_s specific surface area of the compacted material, E the leachate volume fraction, V the volume and A the surface. The mass transfer coefficient k_{SL} is considered non-limitative for the mass transfer between the compacted material and the leachate. Consequently its numeric value was set to a high enough value determined by simulation.

Eqs. (1) and (2) are applied in the case of elements like Na^+ and K^+ coming from soluble salts (halite, sylvie) initially dissolved in the pore water. The diffusion coefficients of Na^+ and K^+ were determined by fitting the diffusion model to the experimental data (concentrations in the leachate) obtained by the CGLT test.

3.2. Column hydrodynamics identification

The coupled geochemical–transport modelling of the percolation process requires the knowledge of the hydrodynamic regime characterised by the dispersivity and the occurrence of stagnant zones. The transport of the aqueous solution in the column is convective–dispersive with a constant flow rate Q . The one-dimensional flow regime can be modelled by a series of N identical open continuous stirred tank reactors (CSTR). The CSTR-series model and the advection–dispersion model commonly used in hydrology give equivalent results [6–8]. The application of a CSTR model has some advantages for the resolution of the system of partially differential equations which becomes ODE-type. The dispersivity of the porous medium of length L is then characterized by the number of tank reactors in the series, N , which value is determined by a tracer response

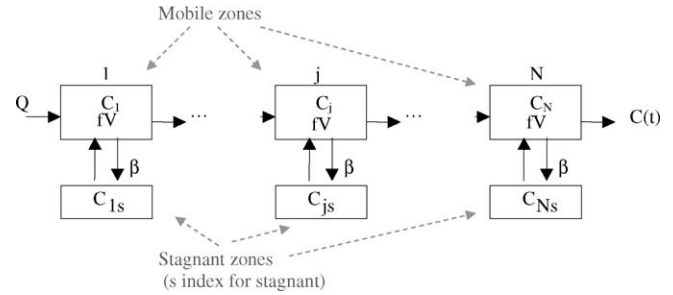


Fig. 3. Convective–dispersive flow model with stagnant zones.

study:

$$\alpha = \frac{L}{2(N-1)} \quad (3)$$

The model of convective–dispersive flow with stagnant zones is presented in Fig. 3. Each reactor j representing the mobile zone of the column exchanges mater with a stagnant zone with a flow defined by βQ with $\beta < 1$.

The balance equations in the mobile and stagnant zones are, respectively:

$$\frac{dC_j}{dt} = \frac{N}{f\tau}(C_{j-1} - C_j) - \frac{1-f}{f} E_f(C_j - C_{js}) \quad (4)$$

$$\frac{dC_{js}}{dt} = E_f(C_j - C_{js}) \quad (5)$$

$$E_f = \frac{\beta N}{\tau(1-f)} \quad (6)$$

where C and C_s are the concentrations of a given species in the mobile and stagnant zones, respectively, f the volume fraction of the mobile zone, β the exchange flow fraction, τ the theoretical residence time (V_0/Q), E_f the global exchange factor. The unknown parameters are: the dispersivity α , the mobile liquid fraction f and the exchange factor E_f . They can be estimated by tracer experiments and fitting the model to the experimental data (tracer concentration at the column outlet). The model was applied to both hydrodynamic experiments performed on the laboratory percolation column and on the pilot column.

3.3. Geochemical modelling

The geochemical modelling was performed with PHREEQC (v2.10) [9] and the MINTeq thermodynamic data base. Literature information about the fly ash mineralogical composition, the elemental total content and the equilibrium experimental results obtained in ANC test were used to build a solid phase model of the fly ash. The mineralogical model and the transport modelling results were both used in PHREEQC to simulate the percolation column experiment and the leaching process on the field pilot.

4. Results and discussions

The experimental results were used in the modelling step in order to determine the main physical and chemical parameters and to explain and assess the leaching behaviour.

Table 1
Elemental composition of the fly ash

Major oxide content (%)		Minor element content (mg/kg)			
SO ₃	0.25	As	50	Ni	115
SiO ₂	57	Ba	1700	Pb	63
Al ₂ O ₃	28.5	Be	7	Sn	<1
Fe ₂ O ₃	6.3	Cd	<1	Sr	870
TiO ₂	1.1	Co	46	Tl	11
CaO	1.7	Cr	220	V	360
MgO	1.7	Cr(VI)	3	Zn	146
K ₂ O	4.3	Cu	140		
Na ₂ O	0.5	Hg	0.4		
P ₂ O ₅	0.4	Mn	515		

4.1. Waste characterisation

The elemental composition of the studied fly ash is summarised in Table 1. The major oxide content confirms the alumino-silicate nature of the waste. Among the potential pollutants, Cr is one of the most abundant and consequently is always detected in the leachates (a soluble fraction being available for leaching). By X-ray analysis were detected as major phases: quartz (SiO₂), mullite (2SiO₂·3Al₂O₃) and periclase (MgO).

4.2. CGLT and the diffusion coefficient

The results of the CGLT test expressed as ion (Na⁺, K⁺) concentration in the leachate were used to model the diffusion transport in the porous system as explained in Section 3.1. The experimental and simulated flux of Na⁺ is shown in Fig. 4. For Na⁺ and K⁺ the diffusion coefficients are similar and equal to $3 \times 10^{-10} \text{ m}^2/\text{s}$.

4.3. Dissolution kinetics

The kinetic study results (Fig. 5) show that the solid/liquid system evolves for the first 10 days. A concentration plateau is

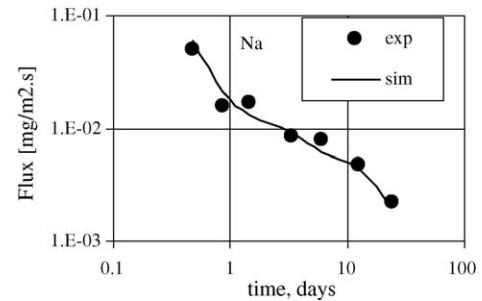


Fig. 4. CGLT experimental and simulated flux of Na⁺.

observed for longer periods. In the experimental conditions characterized by a first contact of the material with water, a closed isolated system and a short time scale, the system was supposed at equilibrium after 10 days. These results do not exclude the possibility of slow dissolution reactions. It is important to underline that the material releases an important soluble fraction during the first contact with water. This process can hide or slowdown certain chemical reactions (for example the initial high Na⁺ concentration resulting from halite dissolution slowdown the albite dissolution).

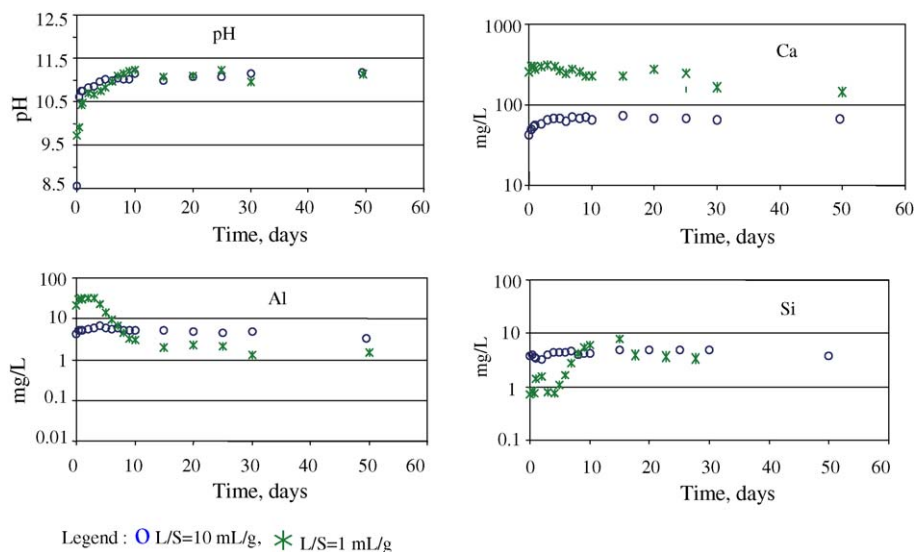


Fig. 5. Dissolution kinetics for several elements and pH evolution in batch system for two L/S.

4.4. ANC and geochemical modelling applied to fresh fly ash

The geochemical model is based on literature information concerning the mineralogical composition of aluminosilicate type fly ashes and on the leaching test data.

The majority of coal fly ashes of thermal processes studied by various authors [10–16] are composed of the following crystalline phases: quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), hematite (Fe_2O_3), magnetite (Fe_3O_4), K-feldspar (KAlSi_3O_8) and Na-feldspar ($\text{NaAlSi}_3\text{O}_8$), lime (CaO), anhydrite (CaSO_4). Other crystalline phases were highlighted by [16]: gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), akermanite ($2\text{CaO}\cdot\text{MgO}\cdot2\text{SiO}_2$), anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), calcium-aluminate ($\text{CaO}\cdot\text{Al}_2\text{O}_3$), tricalcium-aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$). Secondary minerals can be obtained after hydration of ashes, among these minerals can be quoted [17]: portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3), gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot26\text{H}_2\text{O}$), brucite ($\text{Mg}(\text{OH})_2$). Several authors [18–22] affirmed that the leaching of Al is controlled by amorphous $\text{Al}(\text{OH})_3$ for pH ranging between 6 and 9, by gibbsite ($\text{Al}(\text{OH})_3(\text{c})$) for pH higher than 9. Silicon concentration is governed by the solubility of quartz (SiO_2) at pH lower than 10 and by the solubility of wairakite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot2\text{H}_2\text{O}$) at higher pH. Concerning the trace elements the literature is very poor in mineralogical experimental data. On the other hand several hypotheses are given as for their solid speciation. Some of these hypotheses are mentioned below.

The leaching of Cr(VI) can be due to BaCrO_4 and $\text{Ba}(\text{S}, \text{Cr})\text{O}_4$ [23]. A solid solution like $\text{Ba}(\text{S}, \text{Cr})\text{O}_4$ can control the leaching of Cr [18,24]. According to [19] Cr in leachates can be in equilibrium with amorphous or crystalline $\text{Cr}(\text{OH})_3$. The trace elements such as Cr and As can be associated to iron oxides and aluminosilicates [12]. $\text{Ba}_3(\text{AsO}_4)_2$ is the phase suggested controlling the solubility of As(V) [25]. Powellite (CaMoO_4) appeared to control the Mo concentration in extracts with hot water [20]. MoO_4^{2-} forms complexes on iron hydroxide surface as was stated by [26] in the case of municipal solid waste incinerator bottom ashes. The control of the As, Mo, V concentrations was supposed to be due to adsorption/desorption reactions [19]. The leaching of Ba and Sr from fly ash lysimeters is rather controlled by a solid solution ($\text{Ba}, \text{Sr})\text{SO}_4$ than by solid phases like BaSO_4 or SrSO_4 [18]. In the presence of barite (BaSO_4), chromate ion adsorbs with co-precipitation forming solid solutions $\text{Ba}(\text{S}, \text{Cr})\text{O}_4$ with different S/Cr proportions [27]. Such solid solutions can explain for example the leaching of Cr and Ba from steel slag [28]. In conclusion, it is expected that Ba^{2+} , Sr^{2+} , CrO_4^{2-} and SO_4^{2-} exist as complex solid solutions in the fly ash or neo-form solid solutions further to contact with water. It is obvious that the trace element speciation and behaviour is still not fully elucidated.

The ANC test results were used to develop the mineralogical model. The nature of certain solid phases can be identified from the saturation indexes SI calculated for the experimental composition of the solution. Based on the SI results and on the literature mineralogical information a solid model was proposed to simulate the fly ash/demineralised water system. Then the simulation of the other test samples in which acid or base was added per-

mitted to fit the mineralogical model and to semi-quantify the solid phases. The model is based on several hypotheses exposed below.

In the first step of the modelling approach the mineralogical model takes into account phases dissolving relatively rapidly (in less than 10 days). A second modelling step will take into account other test results and mechanisms as explained in Section 4.5.

In the case of metals susceptible to precipitate as hydroxides in the experimental conditions, the most soluble hydroxide was chosen from the data base, accordingly with the priority rule of Ostwald [29]. Some solid phases can dissolve but not precipitate (case of high temperature formed silicates, oxides).

Na and K released in ANC test are supposed to come from soluble phases like halite (NaCl) and sylvite (KCl) because their concentrations are independent of pH (Fig. 6) and relatively important. At the same time, the concentration of Cl solubilised was of the same order of magnitude as the Na and K concentration. The major elements Al and Si are contained in aluminosilicates and silicates incorporating also Ca, Mg, Na, K and other trace elements. Most of these phases have a low solubility and/or very slow dissolution kinetics. However, a more reactive hydrated calcium silicate as okenite ($\text{CaSi}_2\text{O}_4(\text{OH})_2\cdot\text{H}_2\text{O}$) is necessary in the model to account for the buffer capacity of the material. The natural pH of the material is 10.7 (for the experimental conditions $L/S = 10 \text{ mL/g}$). A slightly carbonation of the material is possible. At the natural pH of the material the calcite (CaCO_3) is stable. These Ca-containing phases were quantified by fitting the model to the ANC (pH–mmol H⁺) curve (Fig. 5) and to the Ca concentration–pH curve. A soluble fraction coming from a small quantity of gypsum ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$) can explain the pH-independent concentration of SO_4^{2-} (Fig. 6). Gypsum quantity was estimated from the sulphate concentration. The SI calculation indicated the following phases being in a near equilibrium state with the leachate: brucite ($\text{Mg}(\text{OH})_2$) $\text{SI} = -0.5$, gibbsite ($\text{Al}(\text{OH})_3(\text{c})$) $\text{SI} = 0.01$. The periclase (MgO) detected in the material hydrates to brucite ($\text{Mg}(\text{OH})_2$); its quantity was fitted to the Mg concentration–pH curve (corresponding to the maximum Mg concentration). The gibbsite quantity can be estimated by fitting to the ANC curve in the pH 4 zone.

Concerning the target pollutants, Cr, As, Mo, several reaction types are possible in the context of fly ash–water systems. The elemental analysis of the waste points out that only a small fraction of Cr exists in (VI) valence state. The most quantity may behave as Cr(III) oxides having a very low solubility. The Cr(VI) solid fraction, formed by slow oxidation of Cr(III) species, seems to be responsible of the chromium dissolution by leaching. A relatively soluble phase, BaCrO_4 , was considered.

Arsenic behaves mostly as arsenates AsO_4^{3-} in the redox context of the waste in contact with atmospheric oxygen. The SI calculation indicated the most plausible phases (limited to the data base used) for the trace elements: barite (BaSO_4) $\text{SI} = 0.3$, $\text{BaHAsO}_4\cdot\text{H}_2\text{O}$ $\text{SI} = 0.08$, CaMoO_4 $\text{SI} = -0.9$. $\text{BaHAsO}_4\cdot\text{H}_2\text{O}$ and CaMoO_4 were retained for As and Mo speciation; the maximum quantity of As and Mo dissolved in the ANC test was

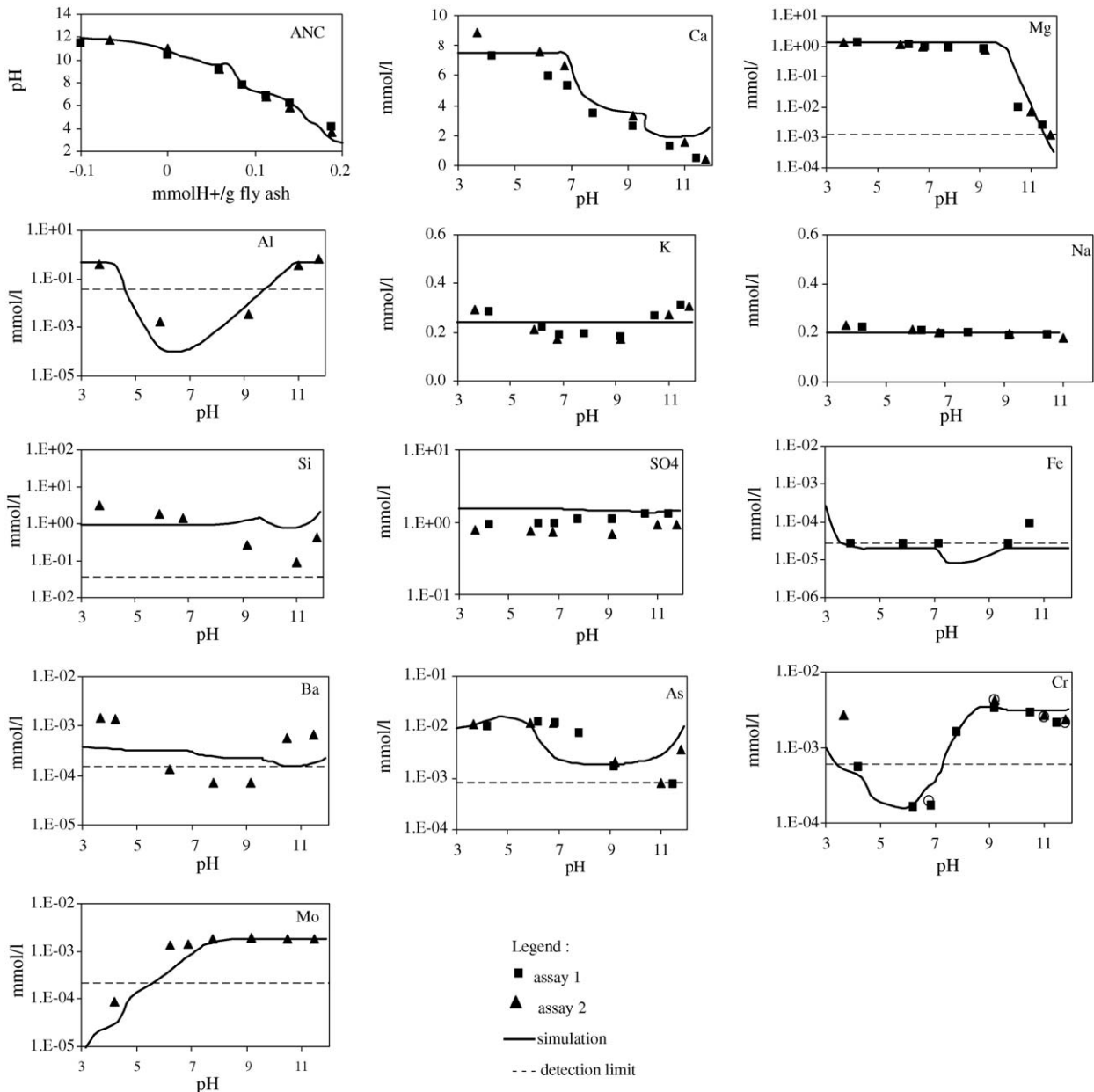


Fig. 6. ANC experimental and simulation results.

considered to estimate the solid phase quantity. Concerning barite, simulation assays performed further for the percolation test showed that the more suitable is to consider a solid solution containing Ba^{2+} , Sr^{2+} , SO_4^{2-} and CrO_4^{2-} instead barite. The reasons will be explained in Section 4.5.

A surface complexation model was added in order to explain the behaviour of As, Cr and Mo at neutral and acidic pH. The diffuse layer model implemented in PHREEQC and the complexation constants of Dzombak and Morel supplied with MINTEQA2 database were used. According to [30] the sorption surfaces on amorphous ferric hydroxide are of two types, i.e. high-capacity/low-affinity and low-capacity/high-affinity, and have a site density of 0.2 mol/mol Fe and 0.005 mol/mol Fe, respectively. In the geochemical model, the ferrihydrite ($\text{Fe}(\text{OH})_3$) surface was equilibrated with the global mineralogical assem-

blage listed in Table 2. The quantity of ferric hydroxide was adjusted to obtain the best concentration simulations for Cr, As and Mo.

Table 2 shows also the fraction of the total content of each element used in the geochemical model. The quantity of several elements like As, Cr(VI), S, Sr taken into account in the model represents 100% of the element total content in the fly ash.

With these considerations the mineralogical model was developed and used to simulate the ANC test by adding aliquots of acid and base to the initial fly ash/water model system. The experimental results for two replicates and the simulation results for all elements are presented in Fig. 6. A good agreement is observed between simulations and experimental data in the case of the neutralisation curve (pH–mmolH⁺/g) and for almost all species concentrations (mmol/L–pH).

Table 2
Solid phases and fraction of element total content considered in the model

Solid phases	mmol/kg fly ash	Element	% of TC
BaCrO ₄	0.05	Al	0.6
BaHAsO ₄ ·H ₂ O	0.7	As	104.9
Periclase (MgO) or brucite (Mg(OH) ₂)	13	Ba	80.7
Calcite (CaCO ₃)	40	Ca	65.5
CaMoO ₄	0.018	Cr	1.4
Ferrihydrite (Fe(OH) ₃)	0.6	Cr(VI)	104.0
Gibbsite (Al(OH) ₃ (c)) ^a	5	Fe	3.0
Gypsum (CaSO ₄ ·2H ₂ O)	10	K	2.9
Halite (NaCl)	2	Mg	3.1
Okenite (CaSi ₂ O ₄ (OH) ₂ ·H ₂ O)	20	Mo	18.8
Portlandite (Ca(OH) ₂)	9	Na	4.2
Solid solution (BaSr)(CrS)O ₄	20	S	100.0
Sylvite (KCl)	2.4	Si	6.4
Al(OH) ₃ (a) ^b	Neo-formation	Sr	100.7
SiO ₂ (a) ^b	Neo-formation		
Kinetic reactants			Parameter
Albite (NaAlSi ₃ O ₈)	23.8		$p_1 = 5 \times 10^4$
K-feldspar (KAlSi ₃ O ₈)	238		$p_1 = 1 \times 10^6$
Ca-Olivine (Ca ₂ SiO ₄)	4.7		$p_1 k_r = 2 \times 10^{-5}$

^a (c) for crystalline.

^b (a) for amorphous.

4.5. Column assays

4.5.1. Column hydrodynamics

The results of the tracer experiments were used to identify the dispersivity and the stagnant zones of the column following the modelling approach described in Section 3.2. The hydrodynamic parameters identified (Table 3) are the dispersivity α , the exchange factor E_f and the mobile volume fraction f .

4.5.2. Coupled geochemical–transport modelling

The hydrodynamic study supplied some of the column characteristics like the stagnant zone parameters (mobile and immobile porosity, exchange factor) and the dispersivity. Considering that these parameters do not change significantly when the liquid velocity changes (always in laminar regime), the parameters necessary to percolation simulation with PHREEQC are thus determined (Table 3).

The experimental results are presented in Fig. 6. The outlet concentrations and the pH were represented in function of

the number of pore volumes, V/V_0 , passed through the column. Three kinetic domains are identified. The first domain up to $V/V_0 = 2$, corresponds to the evacuation of the initial pore water from the mobile porosity (convection–dispersion). The second domain up to $V/V_0 = 20$ corresponds to the evacuation of the immobile porosity charged initially at equilibrium. The third domain shows the fly ash behaviour after the evacuation of the most soluble species. The concentrations remain constant for a long period and generally at a low level; a quasi-permanent regime installs.

Simulation assays with the initial mineralogical model developed for the ANC test were not satisfactory simultaneously for several elements affected by the common ion effect: Ba, Cr, As, S. Barite taken into account initially in the model had to be replaced. A barium sulphate partially substituted by chromate as BaCr0.04S0.96O₄ or BaCr0.23S0.77O₄ (solubility data taken from [28]) was tested but the results were not satisfactory. A solid solution was then proposed starting from barite (BaSO₄), BaCrO₄ and celestite (SrSO₄) and having the composition Ba_{0.5}Sr_{0.5}(CrO₄)_{0.0002}(SO₄)_{0.9998}. In fact it is a double sulphate of barium and strontium in which a small fraction of SO₄²⁻ was substituted by CrO₄²⁻. The long-term release of Na and K and the new pH-plateau at 10 suggested introducing in the mineralogical model of some slow dissolving phases. Albite (NaAlSi₃O₈), K-feldspar (KAlSi₃O₈) and Ca-olivine (Ca₂SiO₄) were introduced as kinetic reactants with a slow dissolution. The kinetic models for albite (NaAlSi₃O₈) and K-feldspar (KAlSi₃O₈) are taken from the LLNL database [31]. For Ca-olivine (Ca₂SiO₄) the general kinetic model implemented in PHREEQC was used [9]:

$$R = p_1 \left(\frac{m}{m_0} \right) k_r (1 - 10^{SI}) \quad (7)$$

Table 3
Column parameters necessary to percolation simulation with PHREEQC

Column parameters	
Darcy's velocity (Darcy) (m/s)	1.7×10^{-6}
Mobile porosity, $f\varepsilon$	0.29
Pores velocity (m/s)	5.8×10^{-6}
Length of the column, L (m)	0.3
Diffusion coefficient, D_a (m ² /s)	3×10^{-10}
Mobil volume fraction, f	0.9
Immobile porosity, $(1 - f)\varepsilon$	0.03
Exchange factor, E_f (s ⁻¹)	1×10^{-7}
Dispersivity, α (m)	0.005

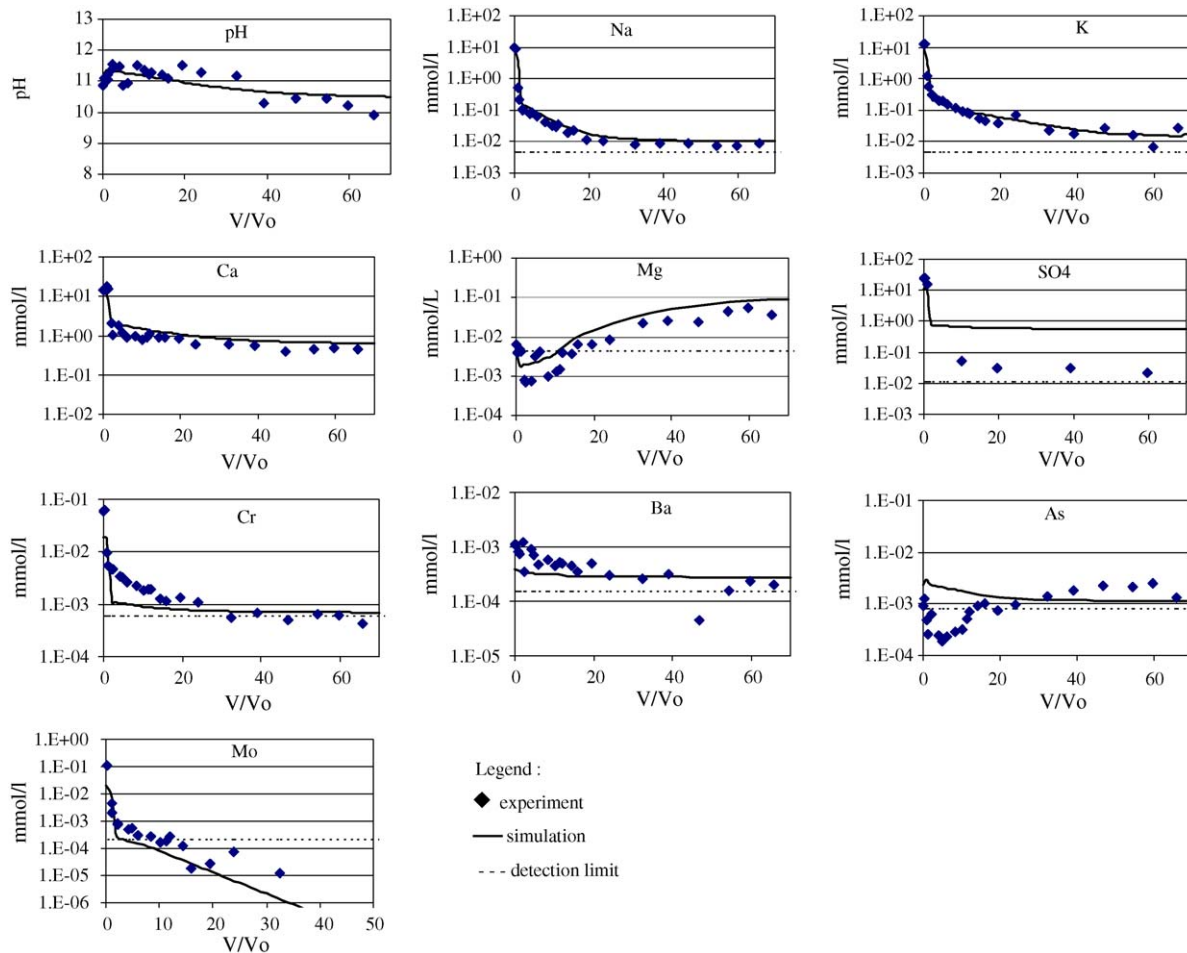


Fig. 7. Percolation column: experimental and simulation results.

where R is the reaction rate, m/m_0 accounts for changes in solid quantity, k_r an empirical constant, p_1 is a specific surface. For albite and K-feldspar k_r is given by [31] and the p_1 parameter was adjusted in order to well simulate the Na and K column concentrations. For Ca-olivine the adjusted kinetic parameter was the product $p_1 k_r$ (Table 2).

The model adjusting for full time scale validity requires an iterative method using alternately the ANC data and the column data until an overall optimum result is obtained. So, the new model comprising kinetic phases and a solid solution was applied once again to ANC data in order to validate it. The final model presented in Table 2 was then used to obtain the simulation results given in Fig. 7 for the column and in Fig. 6 for ANC test. A good agreement is observed between experiments and simulations.

4.6. Field pilot

4.6.1. Hydrodynamic study

The water balance of the lysimeter over 1 year is presented in Table 4. The major part of rainfall is collected after infiltration through the ashes; a small fraction constitutes the runoff. The half of the rainfall was partially retained in the porous system and partially was evaporated. The water percolated through the lysimeter during 18 months corresponded to a liquid/solid ratio of 1.18 L/kg dry ash. The rainfall frequency and the evolution of the infiltrated flow are shown in Fig. 8.

The results obtained by the hydrodynamic experimental study performed on the pilot column were used to determine the main physical parameters necessary to the coupled geochemical-transport modelling. The maximum flow rate of 1.2 mL/min

Table 4
Water balance for the field pilot

Hydrologic balance for the first 12 months		Lysimeter parameters for 18 months	
Total rainfall (L/m ² /year)	856	Fly ash mass/surface (kg/m ²)	600
Run off (%)	2.7	Infiltrated volume/surface (L/m ²)	710
Percolation (%)	44.6	L/S (L/kg)	1.18
Evaporation and retention (%)	52.7		

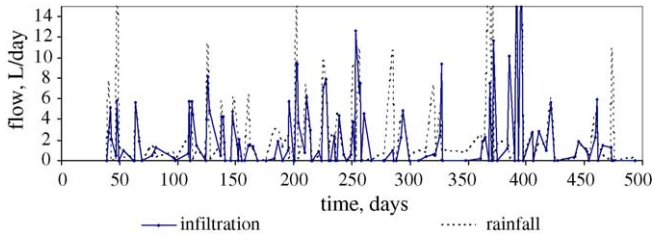


Fig. 8. Rainfall and infiltration flow through the lysimeter.

was imposed by the material permeability which was estimated at 6×10^{-7} m/s. After the stop of the rain flow the discharge of 90% of the total drained water taken about 5 h. The total water volume collected represents only 3% of the total water quantity existing in the column in saturated conditions which demonstrates a high water-retention capacity of the material. The total open porosity was estimated at 0.35 corresponding to a humidity of 27%. The material drained under normal pressure still holds 26% humidity. Concerning the hydrodynamic parameters, the tracer behaviour was simulated using the model described by Eqs. (3)–(6) and the obtained results demonstrated similar behaviour with the laboratory percolation column: a near plug flow with dispersivity $\alpha = 0.001$ m, small stagnant zones (mobile volume fraction $f = 0.97$) with an exchange factor $E_f = 1 \times 10^{-7} \text{ s}^{-1}$. The conclusion of both lab and field scale hydrodynamic experiments is that the compacted fly ash has a high retention capacity, the pores are quasi-saturated in water even during dry periods (if evaporation is not predominant), the water flow is plug like and the drainage very rapid.

4.6.2. Coupled geochemical–transport modelling

The coupled geochemical–transport model for the field pilot is based on the same fly ash mineralogical model. The contact with the atmospheric CO_2 was taken into account for the first period of 40 days in which the compacted fly ash layer was in contact with air and filled in slowly with the rain water (Fig. 8). The mean composition of the rain water locally analysed was also taken into account in the simulation: pH 5.4 due to absorbed CO_2 and of traces of SO_4^{2-} (0.002 mmol/L).

The flow rate of the leachate percolating the ash layer was considered as variable. The total time was divided in periods of maximum and minimum flows corresponding to the diagram in Fig. 8. Mean flow values were estimated and used as constant flows for each period. The PHREEQC model was composed of two steps: at the beginning (40 days) no water flow and equilibration with atmospheric $\text{CO}_2(\text{g})$ were considered, in the second step the material partially carbonated was in contact with rain water which infiltrated with different flows following the rainfall. The simulation was realised for 44 months ($L/S \text{ pilot} = 2.7$), the life time of the field pilot, considering the same rainfall regime as for the first 18 month. The experimental concentrations and pH monitored on the site and the simulation results are shown in Fig. 9. The pollutant concentration simulations are satisfactory given the site conditions and the variability of the ambient parameters, particularly the temperature.

On the same graphs were reported the concentrations measured at the outlet of the laboratory percolation column. The field pH is lower than in the laboratory experiments proving the carbonation of the material during the site works and at the beginning of the natural leaching process. One concludes that chemical factors occurring in real scenarios, like the contact

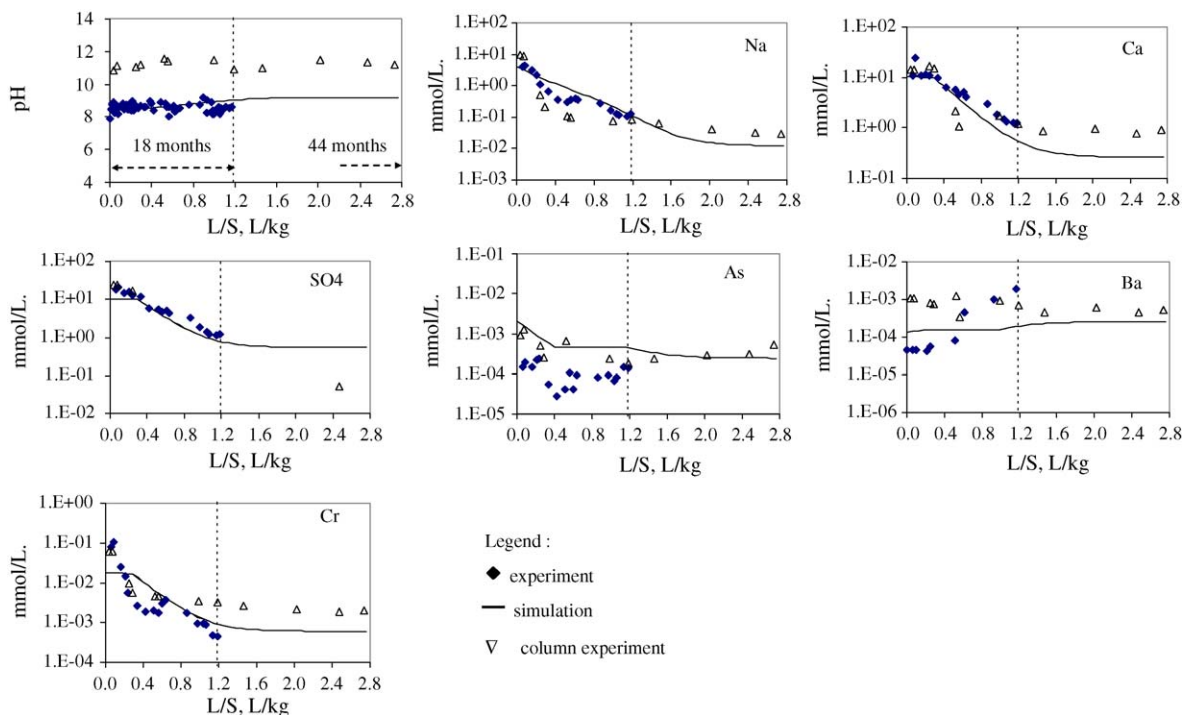


Fig. 9. Released pollutants from the site pilot: experimental and simulations, comparison with the laboratory column results.

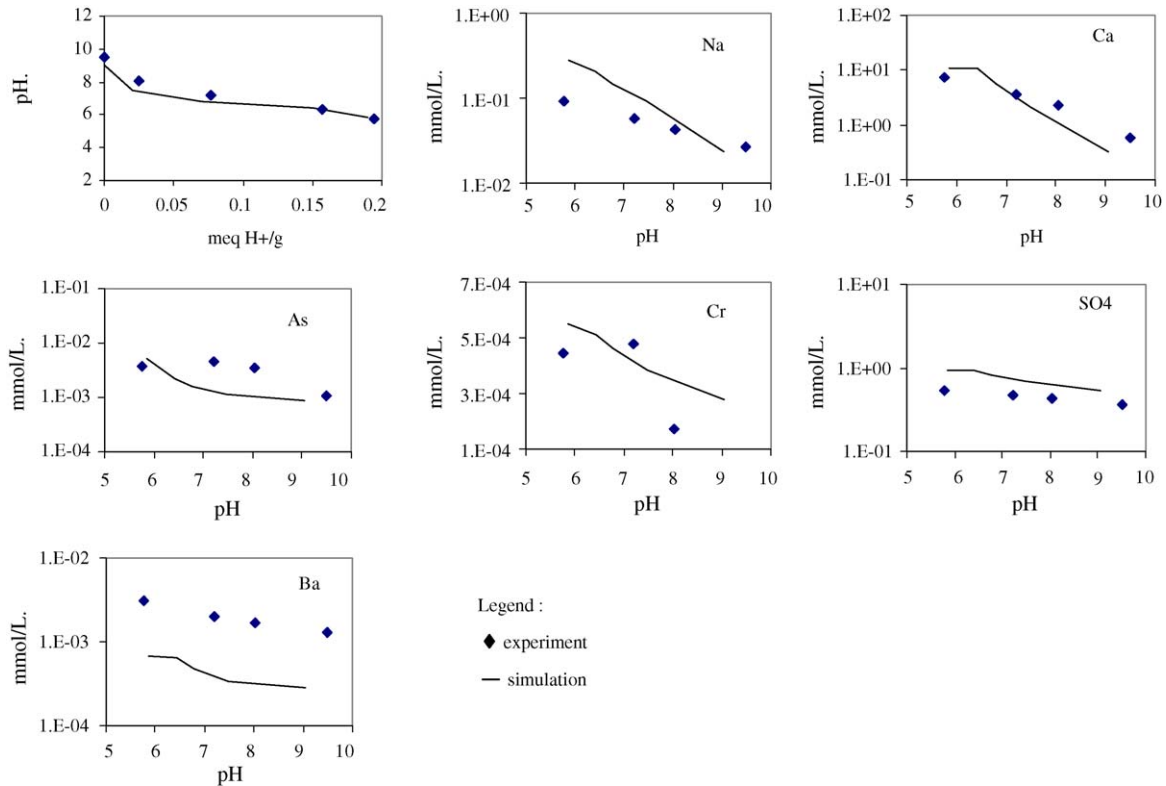


Fig. 10. ANC of the leached fly ash in scenario.

with the atmosphere, lead the system towards a state that cannot be extrapolated from a laboratory experiment (currently standardised leaching tests). In the case of elements contained in a high soluble solid fraction (case of Na^+ , Ca^{2+} , SO_4^{2-} , CrO_4^{2-}) the initial releases ($L/S=0$) in a laboratory column and on the field pilot are scarcely similar. Obviously the initial releases of low soluble elements like As and Ba is different for depending in the pore water chemical context. The pilot release curve exhibits two periods. As in the case of lab-column, the first period corresponds to the evacuation of the soluble fraction initially dissolved in the pore water. But the flush out process is discontinuous due to the alternation of rain periods. In fact periods of convection as dominant transport mechanism (pore water discharge) alternate with periods of diffusion as mainly transport process in the porous system (no water infiltration). The global result in terms of element release is an apparent batch behaviour and not a dispersive-plug one as it may be expected. The extent of the first dynamic period corresponds to 24 months, i.e. $L/S = 1.5$ or $V/V_0 \text{ pilot} = 5$.

4.6.3. ANC test applied to field leached material

The acid neutralisation capacity and the solubility of elements contained in the leached fly ash are different of those determined on the fresh waste. As the Fig. 10 shows, the carbonated material has a natural pH lower and the buffer plateau moved towards pH 7. Generally the element solubility is lower than in the case of fresh waste, for the studied pH domain. The geochemical simulation of ANC results were realised using

the solid model calculated at 44 months of leaching with the geochemical–transport model established for the pilot (the end point of the pilot simulation). The main changes operated by the natural leaching during 44 months were:

- the carbonation of the material—the final CaCO_3 quantity was about 110 mmol/kg fly ash.
- the evacuation of the initially dissolved species in the pore water during the first 24 months.

Salts like sylvite, halite, BaCrO_4 , gypsum were flushed out in the first leaching period. After that, the concentration of elements like As, Ba, Cr, S, was controlled by weak soluble phases, i.e. $\text{Ba}_x\text{Sr}_{1-x}(\text{SO}_4)_y(\text{CrO}_4)_{1-y}$ solid solution and BaHAsO_4 . For the life time of the pilot the quantities of these phases were practically unchanged because of their very low solubility.

The modelling results presented in Fig. 10 generally agree with the ANC experimental data except for Ba. The ANC simulation results and their adequacy with the experimental data account for the geochemical–transport model global validation at least for the time scale of the field pilot.

5. Conclusions

- (1) Peer experimental–modelling tools were developed and applied in the case of coal fly ashes with the aim to assess the leaching behaviour in a use scenario. Laboratory-scale and field pilot experimental studies were performed in order

to identify and quantify the main transport phenomena and chemical processes. A quantitative geochemical model was developed for the fly ash–water system taking into account the equilibrium chemical reactions as well as the kinetic processes. The transport phenomena were integrated into the model at each level. The model was validated by comparison of the simulation results on ANC experimental data obtained on a sample taken on the field pilot after 44 months of leaching under natural conditions.

- (2) Literature data and laboratory experiments were used to develop the geochemical model. One concludes that the concentration of some elements like Ba, S, Cr and As are strongly correlated. Their behaviour is explained by the common ion effect between BaHAsO_4 and a solid solution $\text{Ba}_x\text{Sr}_{1-x}(\text{SO}_4)_y(\text{CrO}_4)_{1-y}$. The soluble CaMoO_4 salt seems to control the Mo concentration. At neutral and acid pH the model of surface complexation on ferric hydroxides was added to dissolution/precipitation model and described very well the behaviour of As, Cr, and Mo.
- (3) At each level the dynamic processes were identified and quantified. During the first contact with water an equilibration time of about 10 days is necessary and has to be considered in all other laboratory experiments (ANC, column percolation). More, at larger time scale a slow dissolution kinetic was identified for silicate phases as albite, K-feldspar or Ca-olivine. The hydrodynamic properties of compacted fly ashes were identified: a high water retention capacity (97% of the pores are water filled after draining under normal pressure), a flow regime close to plug type, a low fraction of stagnant zones (<0.03%). The scenario factors like the carbonation and the rainfall play an important role on the leaching behaviour. The direct extrapolation from lab-scale to field scale can lead to erroneous results if these factors are not accounted for. So the carbonation diminishes the leachate pH from 11 to 8.5. The alternation of rain periods determines an apparent batch behaviour which slows down the outflow of the initial soluble fraction in pore water, if compared with the laboratory percolation column. The extent of the first dynamic period is strongly dependent on the hydrodynamic regime and its concentration level is determined by the soluble fraction of the material. After that, a long-term leaching period follows characterised by a quasi-stationary release flow due to the equilibrium or low rate dissolution of weak soluble phases.

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