



Environmental assessment of waste matrices contaminated with arsenic

F. Sanchez^{a,1}, A.C. Garrabrants^a, C. Vandecasteele^b,
P. Moszkowicz^c, D.S. Kosson^{a,*}

^a Department of Civil and Environmental Engineering, Vanderbilt University, VU Station B-35 1831, Nashville, TN 37235, USA

^b Department of Chemical Engineering, Katholieke Universiteit Leuven, de Croylaan 46, 3001 Heverlee, Belgium

^c LAEPSI, INSA of Lyon, 20 Avenue Albert Einstein, 69100 Villeurbanne Cédex, France

Received 26 July 2001; received in revised form 25 July 2002; accepted 28 July 2002

Abstract

The use of equilibrium-based and mass transfer-based leaching tests has been proposed to provide an integrated assessment of leaching processes from solid wastes. The objectives of the research presented here are to (i) validate this assessment approach for contaminated soils and cement-based matrices, (ii) evaluate the use of diffusion and coupled dissolution–diffusion models for estimating constituent release, and (iii) evaluate model parameterization using results from batch equilibrium leaching tests and physical characterization. The test matrices consisted of (i) a soil contaminated with arsenic from a pesticide production facility, (ii) the same soil subsequently treated by a Portland cement stabilization/solidification (S/S) process, and (iii) a synthetic cement-based matrix spiked with arsenic(III) oxide. Results indicated that a good assessment of contaminant release from contaminated soils and cement-based S/S treated wastes can be obtained by the integrated use of equilibrium-based and mass transfer-based leaching tests in conjunction with the appropriate release model. During the time scale of laboratory testing, the release of arsenic from the contaminated soil matrix was governed by diffusion and the solubility of arsenic in the pore solution while the release of arsenic from the cement-based matrices was mainly controlled by solubilization at the interface between the matrix and the bulk leaching solution. In addition, results indicated that (i) estimation of the activity coefficient within the matrix pore water is necessary for accurate prediction of constituent release rates and (ii) inaccurate representation of the factors controlling release during laboratory testing can result in significant errors in release estimates.

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Keywords: Leaching; Arsenic; Cement matrices; Contaminated soils; Diffusion modeling

* Corresponding author. Tel.: +1-615-322-1064; fax: +1-615-322-3365.

E-mail addresses: florence.sanchez@vanderbilt.edu (F. Sanchez), david.kosson@vanderbilt.edu (D.S. Kosson).

¹ Co-corresponding author. Tel.: +1-615-322-5135; fax: +1-615-322-3365.

Nomenclature

C_0	initial leachable concentration (mass/m ³)
D_e	effective diffusivity (m ² /s)
D_m	molecular diffusivity (m ² /s)
D_{obs}	observed diffusivity (m ² /s)
LS	liquid-to-solid ratio per gram of dry sample (mL/g dry sample)
LS _a	liquid-to-solid ratio per exposed surface area (cm ³ of leachant/cm ² of exposed surface area) or (cm)
M_a	cumulative mass of the constituent released per unit surface area (mass/m ²)
S_{As}, S_{Ca}	solid phase concentration of arsenic or calcium, respectively (mg/cm ³ of porous matrix)
t	time interval (s)
$y_{i,exp}$	experimental flux at the i th leaching period (mass/m ² s)
$y_{i,sim}$	simulated flux at the i th leaching period (mass/m ² s)

Greek letters

ε	porosity (%)
ρ	density on a dry basis (g dry/cm ³)
τ	tortuosity factor
τ_{MQ}	Millington–Quirk tortuosity factor

1. Introduction

Characterization of waste constituent leaching behavior is a crucial step in the environmental assessment of reuse or disposal scenarios. Recent emphasis on improved knowledge of the long-term behavior and eco-compatibility of wastes has resulted in the need for new evaluation tools and interpretation protocols. In this framework, research programs have been on-going in Europe and the United States to develop a methodology for evaluating the release of inorganic constituents from solid wastes (e.g. industrial wastes, contaminated soils or stabilized/solidified wastes). This methodology is comprised of leaching test methods and interpretation protocols, which emphasize the integrated use of fundamental leaching parameters and release scenario conditions to estimate constituent release [1–6].

Measurement of fundamental leaching parameters (i.e. availability, solubility as a function of pH, constituent release rates, etc.) uses two types of leaching tests: equilibrium-based and mass transfer-based leaching tests. Equilibrium-based leaching tests, typically conducted on crushed materials, aim to measure contaminant release related to specific chemical conditions (i.e. pH, liquid-to-solid ratio). Mass transfer-based leaching tests, carried out on monolithic or compacted granular materials, aim to determine pollutant release rates by accounting for both chemical and physical properties of the material. Several

specific leaching test methods have been developed and are presented elsewhere [5–11]. Interpretation protocols based on the use of behavioral models provide long-term contaminant release estimates for a specified time frame in conjunction with consideration of site-specific and management scenario information. Several leaching models have been developed or are under development to describe the release of constituents of potential concern from waste materials. Long-term assessment using the semi-infinite diffusion model [2,5] assumes that mass transfer occurs solely due to concentration gradients within the matrix. More sophisticated models are required to provide understanding of the phenomena involved during leaching when diffusion alone cannot be assumed to describe mass transport. These models allow for (i) possible species depletion [12,13], (ii) chemical interactions such as dissolution/precipitation phenomena [14–26], (iii) matrix heterogeneity [27] and (iv) external stresses likely to be encountered in the field such as carbonation [28] or intermittent wetting under varied environmental conditions [29,30]. Models incorporating chemical interactions generally describe the solid/liquid equilibrium in porous materials through the progression of solid phase depletion fronts in relation to local pH values. Changes in local pH have been represented in terms of inward diffusion of acid species into the alkaline depleted leached shell [18,20,21] or by the dissolution of calcium hydroxide and the release of hydroxide ions from the matrix [22,25]. Chemical interactions have been modeled using geochemical speciation modeling [16,17,31,32] or experimental solubility data [24,33]. Application of these interpretation protocols and models for estimation of long-term release is dependent on an accurate understanding and representation of leaching mechanisms. This requires validation of the consistency of results between different types of test methods, wastes, model selection and model parameterization.

The objectives of the presented research are to (i) validate the integrated use of equilibrium-based leaching tests and mass transfer-based leaching tests on soils and cement-based matrices contaminated with arsenic, (ii) evaluate the use of diffusion and coupled dissolution–diffusion models for estimating constituent release, and (iii) evaluate model parameterization using results from batch equilibrium leaching tests and physical characterization. The test matrices of concern consisted of (i) a soil contaminated with arsenic from a pesticide production facility (“untreated As soil”), (ii) the same soil subsequently treated by a Portland cement stabilization/solidification process (“S/S treated As soil”), and (iii) a synthetic cement-based matrix spiked with arsenic(III) oxide (“S/S As₂O₃ matrix”). Intrinsic leaching parameters (i.e. acid neutralization capacity of the matrix, arsenic solubility as a function of pH, arsenic availability, physical and chemical properties of the pore water of the porous matrices and constituent release rates from monolithic leach tests) were measured. Evaluation of constituent release was then carried out using the (i) diffusion model [2,12] for sodium and chloride (i.e. highly soluble species), and the (ii) coupled dissolution–diffusion model [25] for arsenic (i.e. species whose solubility exhibits a strong dependence on pore water pH). The coupled dissolution–diffusion model is based on the dissolution and release of calcium hydroxide as the driving factor for controlling the pH within the matrix. Pore water solubility is simulated using experimental solubility data to describe the pore water chemistry of the matrix of concern. A similar assessment approach has been previously validated on cement-based matrices contaminated with lead [33].

Table 1
Properties of the untreated arsenic contaminated soil

Cation exchange capacity (meq./100 g)	28.82
Organic matter (%OM)	21.04
Organic carbon (%OC)	12.21
Total Kjeldahl nitrogen (%TKN)	0.04
Sand (%)	74
Silt (%)	20
Clay (%)	6
Moisture content ($103 \pm 2^\circ\text{C}$) (%)	18
Soil texture	Loamy sand
Total elemental content (mg/kg)	
As ^a	24,400
Ca ^a	12,100
Cl ^a	1,010
Cu ^b	17,460
Fe ^a	60,060
Na ^a	6,460
Mn ^a	440
Pb ^b	1,860
Zn ^b	3,490

^a By neutron activation analysis.

^b By X-ray fluorescence.

2. Materials and methods

2.1. Materials

Properties and elemental content for the untreated As soil are reported in Table 1. The S/S treated As soil, prepared at Rutgers University (NJ, USA) was obtained by mixing 22.2 wt.% ordinary Portland cement, 22.2 wt.% water and 55.6 wt.% untreated As soil. The S/S As₂O₃ matrix, prepared at INSA of Lyon (France) was obtained by mixing 33 wt.% ordinary Portland cement, 13.2 wt.% water, 51.8 wt.% sand, 1 wt.% arsenic(III) oxide and 1 wt.% sodium chloride. The resulting arsenic concentrations for the untreated As soil, the S/S treated As soil and the S/S As₂O₃ matrix were ca. 2.4 wt.%,² ca. 1.4 wt.% (see footnote 1) and ca. 0.9 wt.% (see footnote 1), respectively. The S/S treated As soil samples were molded as cylinders of 10 cm diameter by 10 cm height and cured in the molds for 3 months before removal for testing. The S/S As₂O₃ samples were cast as 15 cm × 20 cm × 10 cm blocks and stored at room temperature in sealed plastic bags. After 28 days of curing, cylindrical cores of 4 cm diameter were taken from the cast blocks and cut into experimental samples with 2 cm height. Fragments of the blocks were saved in sealed plastic bags as source material for tests on crushed materials.

² Dry basis (based on moisture content measured at $103 \pm 2^\circ\text{C}$).

2.2. Measurement of matrix alkalinity and arsenic solubility as a function of pH

Matrix alkalinity and arsenic solubility as a function of pH was measured for the three test matrices. The methods used were predecessors to the current CEN TC 292 characterization of waste—leaching behavior test—pH dependence test with initial acid/base addition protocol [34] and SR002.1 (alkalinity, solubility and release as a function of pH) protocol [5]. Series of parallel extractions of aliquots of finely crushed material (i.e. <300 μm) were carried out at liquid-to-solid (LS) ratio of 10 mL/g (S/S As_2O_3 matrix) or 5 mL/g (untreated and S/S treated As soils). The extractants were aqueous solutions over a range of nitric acid or potassium or sodium hydroxide concentrations as required to achieve final solution pH between 2 and 12. After a contact time of 24 h with agitation, the leachates were filtrated through 0.45 μm pore size polypropylene membranes and the leachate pH of each extract was measured. Filtered leachates then were preserved with nitric acid to pH <2 for chemical analyses.

The neutralization behavior of each material to both acid and base was evaluated in terms of the pH of each extract as a function of milli-equivalents of acid or base added per gram of dry solid. Arsenic concentration of each extract was plotted as a function of extract final pH to provide solubility as a function of pH. In addition, arsenic oxidation state and speciation were investigated in the leachates of the untreated and S/S treated As soil. Three analytical methods were used to determine the oxidation state of arsenic [35]: (i) inductively coupled plasma atomic emission spectrometry (ICP-MS) for total arsenic concentration, (ii) hydride-generation ICP-MS for As(III) concentration, and (iii) capillary zone electrophoresis providing both As(III) and As(V) concentrations.

2.3. Measurement of arsenic availability

Two test methods were used to determine the availability of arsenic of both untreated and S/S treated As soils: the availability test method at pH 4.0 and 8.0 [7] and the availability test method at pH 7.0 with ethylenediamine-tetraacetic acid (EDTA) [36]. These protocols were designed to measure the maximum quantity, or the fraction of the total constituent content, of inorganic constituents in a solid matrix that potentially can be released from the solid material.

The availability test method at pH 4.0 and 8.0 consists of two parallel extractions of aliquots of crushed material (<300 μm) at an LS ratio of 100 mL/g dry sample and with a single addition of either nitric acid or potassium hydroxide to achieve a final pH of 4.0 and 8.0. The pH target value of 4.0 and 8.0 aimed to optimize the extraction of cations and anions, respectively. For the availability test method at pH 7.0 with EDTA, an aliquot of crushed material (<300 μm) is contacted at an LS ratio of 100 mL/g dry sample with a solution of 50 mM EDTA at pH 7.0. This extraction fluid is used to chelate metals of interest in solution at near neutral pH during a single extraction. The final specified pH value of 7.0 is obtained by addition of a pre-determined equivalent of acid or base prior to the beginning of the extraction. The amount of acid or base required to obtain the final endpoint pH value is specified by a titration pretest of the material using 50 mM EDTA solution as the titration solution. For both availability tests, the leachate pH was measured prior to filtration through 0.45 μm pore size polypropylene membranes after a contact time

of 24 h with agitation. The filtered leachates then were analyzed for arsenic using flame atomic absorption spectrometry (FAAS).

2.4. Estimation of the physical and chemical properties of the pore water solution of the matrices

Cement matrices and soils are porous media partially saturated with water. The solution filling the pore (i.e. pore water) locally approaches thermodynamic equilibrium with the different constituents of the cement matrix or the soil. The resulting pore water solution may be saturated with respect to some matrix constituents, resulting in deviations from ideal dilute solution behavior and species activity coefficients significantly different from unity. Estimation of the activity coefficient within the pore water is necessary for accurate prediction of constituent solubility within the pore water and coupled mass transfer rates for leaching. The composition of the matrix pore water was evaluated for the three test matrices. The initial concentrations of the major ions in the pore water (hydroxide, sodium, potassium and chloride) were extrapolated from solubility data based on extractions with deionized water at different low LS ratios. For the untreated and S/S treated As soil, aliquots of finely crushed materials (i.e. <300 μm) were contacted for 24 h, at room temperature ($20 \pm 1^\circ\text{C}$) at LS ratio of 10, 8, 6, 4, 2 and 1 mL/g of dry solid. For the S/S As_2O_3 matrix, finely crushed material (i.e. <300 μm) was contacted for 6 h, at room temperature ($23 \pm 1^\circ\text{C}$) with deionized water at LS ratio of 2 mL/g solid (as cured basis). For all extractions, the solid and liquid phases were separated using vacuum filtration through 0.45 μm pore size polypropylene membranes, pH values were measured and the leachates were preserved with nitric acid to pH <2 for chemical analysis. The filtered extracts for the untreated and S/S treated As soil were analyzed for sodium and potassium using FAAS. The filtered extracts of the S/S As_2O_3 matrix were analyzed for sodium and potassium using inductively coupled plasma atomic emission spectrometry (ICP-AES) and for chloride using ion chromatography (IC).

Concentrations of constituents of concern (sodium, potassium and chloride) and pH as a function of LS ratio then were extrapolated to the LS ratio for the pore water within the matrix. The pore water LS ratio is defined by the porosity and density of the matrix as

$$\text{LS} = \frac{\varepsilon}{\rho_{\text{dry}}} \quad (1)$$

where LS is the liquid-to-solid ratio on a dry weight basis (mL/g dry sample), ε the porosity (cm^3/cm^3) estimated from the moisture content of the material, and ρ_{dry} is the density on a dry basis ($\text{g dry}/\text{cm}^3$).

The resulting concentrations then were used to estimate the pore water ionic strength of the three matrices and activity coefficients as a function of the ion charge number.

2.5. Assessment of dynamic release

2.5.1. Mass transfer leaching tests

The test methods used to assess the dynamic of the release of arsenic and major species (i.e. sodium, chloride and calcium) from the three test matrices are predecessors to the current MT001.1 (mass transfer rates in monolithic materials) and MT002.1 (mass transfer

rates in granular materials) protocols [5] and are analogous to NEN 7345 [37] and methods under development by CEN/TC 292.³ Under the conditions of these test methods, leachate pH is dictated by the release of constituents from the matrix being tested. No external pH control was imposed on the system.

The untreated As soil at optimum moisture was compacted to a height of approximately 8 cm into a 10-cm diameter mold using a modified Proctor compactive effort [38]. During leach testing, only the top surface of the compacted material was exposed to the leachant. In addition, the exposed face was covered with a monolayer of 3-mm diameter glass beads in order to prevent surface wash-off. The layer of glass beads was assumed not to contribute significant resistance to diffusion in contrast to the compacted soil because of the relatively inert and porous layer formed. Each compacted sample (i.e. three cylinders of 10-cm diameter by ca. 8-cm height) was contacted with deionized water using a liquid to surface area (LS_a) ratio of 10 mL of leachant/cm² of exposed surface area (LS_a ratio of 10 cm). The leachant was refreshed with an equal volume of deionized water at cumulative leaching times of 3, 6, 12 h, and 1, 4 and 8 days. This schedule resulted in six leachates with leaching intervals of 3, 3, 6, 12 h, and 3 and 4 days.

For the S/S treated As soil, three molded cylinders of 10-cm diameter by 10-cm height were contacted with deionized water using a LS_a ratio of 10 cm. The leachant was refreshed with an equal volume of deionized water at cumulative times of 3, 6 and 12 h, 1, 2, 4 and 8 days. Then the leachant was refreshed every week or every other week up to a cumulative leaching period of 2 months. Beyond this time, leachant was refreshed every month or every 2 months up to a cumulative leaching period of 6 months. This schedule resulted in 17 leachates with leaching intervals of 3, 3, 6, 12 h, 1, 2, 4, 6 days, 1, 1, 1, 2, 1, 1 weeks, 1, 1 and 2 months.

Finally, for the S/S As₂O₃ matrix, fresh cut monolithic samples of 4-cm diameter and 2-cm height were contacted with deionized water using a liquid–solid ratio of 10 mL of leachant/g of sample (i.e. LS_a ratio of ca. 11 cm). The leachant was refreshed with an equal volume of deionized water at cumulative leaching times of 3, 8 h, 1, 2, 4, 7, 11, 18 days, 1, 2, 3, 4, 5, 6 and 8 months. This schedule resulted in 15 leachates with leaching intervals of 3, 5, 16 h, 1, 2, 3, 4 days, 1, 2, 3, 4, 4, 6, 6 and 8 weeks.

For all tests, the leachates were filtrated through 0.45 μm pore size polypropylene membranes and leachate pH was measured at the end of each extraction interval. The leachates then were preserved with nitric acid to pH <2 for chemical analysis. The untreated As soil leachates were analyzed for sodium and arsenic using FAAS. The S/S treated As soil leachates were analyzed for sodium and calcium using FAAS and arsenic using graphite furnace atomic absorption spectrometry (GFAAS). The S/S As₂O₃ matrix leachates were analyzed for sodium, calcium and arsenic using ICP-AES and chloride using ion chromatography.

2.5.2. Release modeling

Constituent release was evaluated following the assessment protocol presented in Fig. 1. The diffusion model [2,12] was used to simulate the leaching behavior of sodium from all

³ CEN/TC 292 is the European Standardization Organization (CEN) technical committee dealing with characterization of waste (established in 1993).

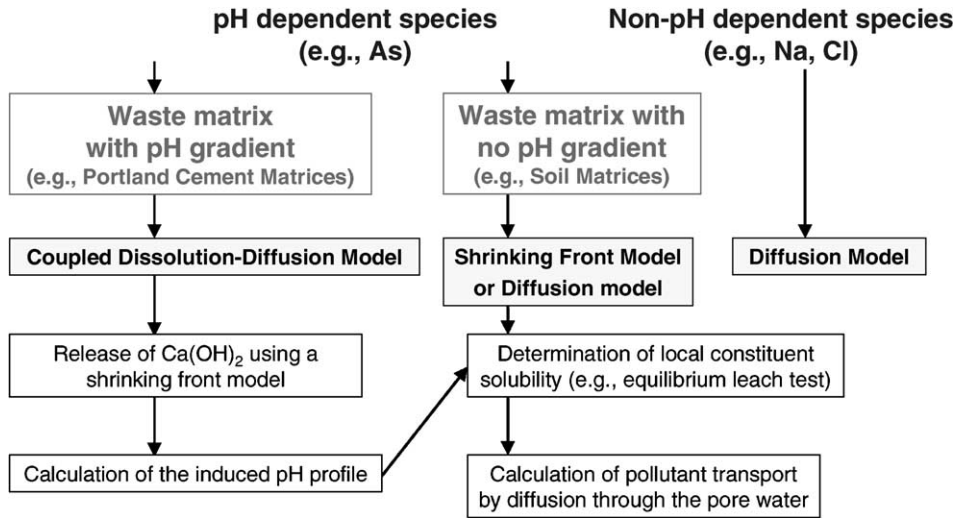


Fig. 1. Assessment protocol for release modeling.

three test matrices and chloride from the S/S As₂O₃ matrix. Previous studies [12,24,25,39] have shown that the diffusion model is well-adapted to describe the release of these highly soluble species. This model, based on Fick's second law, assumes that the species is initially present throughout the homogeneous porous medium at uniform concentration and considers that mass transfer takes place in response to concentration gradients in the pore water solution of the porous medium. Two parameters characterize the magnitude and rate of the release: C_0 , the initial leachable concentration (i.e. available release potential) and D_{obs} , the observed diffusivity of the species in the porous medium. When the species of concern is not depleted over the time period of interest, the cumulative mass release can be described by a one-dimensional semi-infinite diffusion model and calculated considering that the concentration at the solid-liquid interface is equal to zero (i.e. case of a sufficient water renewal, infinite bath assumption) as [40]

$$M_a = 2C_0 \left(\frac{D_{\text{obs}}t}{\pi} \right)^{1/2} \quad (2)$$

where M_a is the cumulative mass of the constituent released per unit total surface area (mg/m^2), C_0 the initial leachable concentration on a total volume basis (mg/m^3), t the time interval (s), and D_{obs} is the observed diffusivity of the species of concern through the overall matrix (m^2/s).

For cases where edge effects are significant or the concentration of the species of concern is reduced over the time period of interest such that the assumption of a semi-infinite media is not valid, a three-dimensional diffusion model is required to estimate cumulative release [12,13].

The coupled dissolution-diffusion model [22,25] was used to simulate the leaching behavior of calcium and arsenic from the two S/S matrices (i.e. S/S treated As soil and

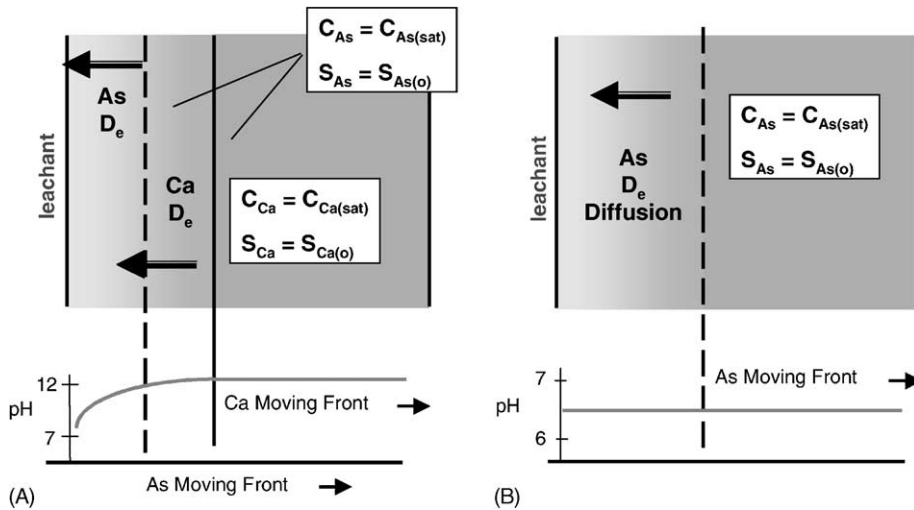


Fig. 2. Moving fronts and concentration gradients established during leaching: (A) Portland cement-based matrices and (B) soil matrices.

S/S As_2O_3 matrix) and the leaching behavior of arsenic from the untreated As soil. For porous matrices containing calcium hydroxide and the pollutant of interest (e.g. Portland cement-based solidified waste like the S/S treated As soil and S/S As_2O_3 matrix), three zones separated by two moving fronts (i.e. dissolution fronts of calcium and pollutant of interest) can be identified within the matrix Fig. 2(A)).

- (i) A first zone, near the matrix–leaching solution interface, in which the solid forms of calcium and pollutant have been dissolved. Calcium and the pollutant of concern in the pore water are then transported by diffusion towards the leaching solution.
- (ii) A second zone, in which calcium hydroxide has been depleted while the solid form of pollutant is still present and in which the matrix pore water is therefore saturated with respect to the pollutant of interest. Calcium, used as an indicator of hydroxide mobility, is transported by diffusion inducing a pH gradient within the pore solution. Local concentrations of the pollutant of interest vary in the pore water and in the solid phase according to the varying solubility of the pollutant due to changes in pH.
- (iii) A third zone, in which the solid forms of calcium and pollutant of interest have not been depleted. In this zone, the pore solution is saturated with respect to all constituents and there is no mass transfer.

The coupled dissolution–diffusion model divides the release computation into several stages: (i) release of calcium hydroxide using a shrinking core model, (ii) calculation of the induced pH profile assuming that local thermodynamic equilibrium occurs in the pore water, (iii) determination of local pollutant solubility from experimental results (i.e. equilibrium leaching tests) and (iv) calculation of pollutant transport by diffusion through the pore water.

For porous matrices containing the pollutant of interest as precipitated solid and in which no pH gradient occurs during leaching (e.g. soil matrices like the untreated As soil), two zones can be identified within the matrix separated by one moving front (i.e. dissolution front of the pollutant of interest) Fig. 2(B)).

- (i) A first zone, near the matrix–leaching solution interface, in which the solid form of the pollutant of concern has been depleted and the pollutant in the pore water is transported by diffusion towards the leaching solution.
- (ii) A second zone, near the matrix core, in which there is no mass transfer and in which the pore water is saturated with respect to the pollutant. In the absence of a pH gradient within the matrix during the leaching, the pollutant saturation concentration remains constant throughout the undissolved core and is identical to the measured pollutant solubility at the natural pH of the matrix of concern.

In the absence of strong pH gradients, the coupled dissolution–diffusion model is similar to a shrinking front model. The modeling process divides the release computation into two stages: (i) determination of local pollutant solubility at the natural pH of the matrix from experimental results (i.e. equilibrium leaching tests), and (ii) calculation of pollutant transport by diffusion through the pore water.

The coupled dissolution–diffusion model requires the knowledge of several parameters for its resolution including the (i) matrix porosity, (ii) solid phase concentrations of constituents of interest (e.g. pollutant and calcium hydroxide concentration), (iii) constituent solubility as a function of pH, (iv) activity coefficient of the pollutant of concern, and (v) effective diffusivity within the porous medium for each species of interest. For each matrix of concern (i.e. untreated As soil, S/S treated As soil and S/S As₂O₃ matrix), the values of these parameters were initially set to values obtained from experimental data. Thus, for the untreated and S/S treated As soil, the matrix porosity was set to the value estimated from the matrix density and moisture content, and for the S/S As₂O₃ matrix, to the value obtained by mercury intrusion analysis. The concentration of calcium hydroxide for both S/S matrices was set to the value estimated from measurement of matrix alkalinity. The initial solid content of arsenic was set to the initial leachable concentration for each matrix. The solubility of arsenic as a function of pH was set to experimentally measured values. In addition, the local arsenic solubility for the untreated As soil was set to the value experimentally obtained at the natural pH of the soil. The activity coefficient of arsenic in all matrices was set to the value estimated from extractions at low LS ratio. Finally, initial values for the effective diffusivities of calcium and arsenic species were determined based on respective literature values of molecular diffusivity [41,42] corrected by a tortuosity factor, τ , representing physical retardation using the following representation:

$$D_e = \frac{D_m}{\tau} \quad (3)$$

where D_e is the effective diffusivity of the species of concern through the overall matrix (m²/s), D_m the molecular diffusivity of the species of concern (m²/s), and τ is the tortuosity factor.

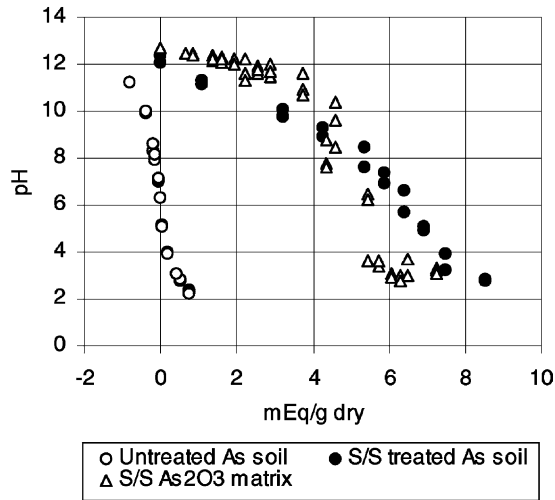


Fig. 3. Acid neutralization capacity curves—comparison of untreated As soil, S/S treated As soil and S/S As₂O₃ matrix.

In turn, the tortuosity factor may be estimated from the Millington–Quirk tortuosity, τ_{MQ} , for a saturated matrix [43] and the matrix porosity⁴ as $\tau = \varepsilon \tau_{MQ} = \varepsilon \varepsilon^{-4/3} = \varepsilon^{-1/3}$, where τ_{MQ} is the Millington–Quirk tortuosity [44] and ε is the matrix porosity.

Simulation results were fit to the experimental results by regressing first species activity coefficient and then the effective diffusivity until the model provided the best fit to the data based on the minimization of the standard error (S.E.). The standard error is a function of the sum of the relative squared error (SRSE) [45] and is defined as follows:

$$S.E. = \sqrt{\frac{SRSE}{n - m}} \quad \text{with} \quad SRSE = \sum_{i=1}^n \left(\frac{[y_{i,exp} - y_{i,sim}]^2}{y_{i,exp}^2} \right) \quad (4)$$

where n is the number of points, m the number of parameters, $y_{i,exp}$ the logarithm of the experimental flux at the i th leaching period, and $y_{i,sim}$ is the logarithm of the simulated flux at the i th leaching period.

3. Results and discussion

3.1. Matrix alkalinity and arsenic solubility as a function of pH

Acid neutralization capacity curves of the test matrices are compared in Fig. 3. The buffering capacity of the untreated As soil was small (i.e. only 0.8 meq. of acid/g of dry

⁴ The Millington–Quirk tortuosity, τ_{MQ} , accounts for physical retardation in the pore structure when calculating a proportionality constant (i.e. an effective diffusivity) between flux based on total cross-sectional area and a concentration gradient based on pore volume. The effective diffusivity used in the coupled dissolution–diffusion model is based on a tortuosity factor, τ , which differs from the Millington–Quirk tortuosity by a factor of porosity.

solid was needed to achieve pH 2) with a natural pH around 6. The low buffer capacity indicates that significant inert material was present in the soil mineralogy. Considerable buffering capacity was provided by calcium hydroxide production during hydration for materials treated by S/S. Thus, ca. 7 meq. of acid/g of dry solid was needed to achieve pH <3 for both S/S treated As soil and S/S As₂O₃ matrix. Nevertheless, the S/S treated As soil showed less buffering capacity than the S/S As₂O₃ matrix at pH values higher than 8 and greater buffering capacity at pH values <8. This shift in neutralization behavior can be explained by differences in (i) cement percentages used (i.e. ca. 22 wt.% for the S/S treated As soil while ca. 33% for the S/S As₂O₃ matrix), (ii) type of cement used (i.e. OPC type I for the S/S treated As soil and CPA-CEM I for the S/S As₂O₃ matrix), (iii) type of waste mixed with the cement and (iv) cement to waste ratio used (i.e. ca. 0.4 for the S/S treated As soil and ca. 0.6, when including the sand, for the S/S As₂O₃ matrix).

Based on the acid addition required to reach pH 11.9 (the pH theoretically reached after complete neutralization of calcium hydroxide), calcium hydroxide produced during the hydration reactions of the cement was estimated at ca. 16 kg/m³ of porous medium (ca. 3% of the hydrated cement paste) for the S/S treated As soil and ca. 230 kg/m³ of porous medium (ca. 21% of the hydrated cement paste) for the S/S As₂O₃ matrix. The low production of calcium hydroxide for the S/S treated As soil compared to quantities generally produced during a Portland cement hydration (i.e. between 20 and 30% [46]) reflected that part of the alkalinity was neutralized during the preparation of the material, perhaps due to reactions of silica in the soil with calcium hydroxide and the relatively low cement to waste ratio used (ca. 0.4).

Arsenic solubility in the three matrices as a function of leachate pH exhibited three different behaviors (Fig. 4). For the untreated As soil, arsenic solubility as a function of pH showed amphoteric behavior with a solubility minimum of ca. 60 mg/L reached around pH 5. Treatment of the arsenic soil with Portland cement resulted in significant reduction

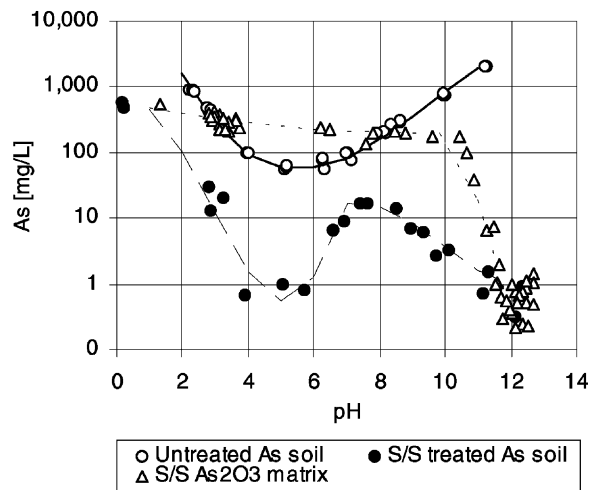


Fig. 4. Arsenic solubility as a function of pH—comparison of untreated As soil, S/S treated As soil and S/S As₂O₃ matrix.

of the arsenic solubility and a significant change of behavior related to modifications of chemical speciation due to lime addition associated with cement hydration. Thus, arsenic solubility of the S/S treated As soil showed a maximum solubility of ca. 20 mg/L in the pH range 6–12 reached around pH 7 and a solubility minimum of ca. 1 mg/L in the pH range 2–6 reached around pH 5. Study of arsenic oxidation state carried out on the leachates obtained from the untreated As soil and the S/S treated As soil showed that most of the arsenic (i.e. 99%) was present in the leachates as arsenate (oxidation states of +5) for both materials. According to the literature [47], the predominant species of As(V) is AsO_4^{3-} for $\text{pH} > 12.5$, HAsO_4^{2-} for pH between 7.3 and 12.5 and H_2AsO_4^- for pH between 3.6 and 7.3. However, the mineral species of the soil and the solubility controlling solid phase were not specifically determined. In the S/S As_2O_3 matrix, arsenic solubility significantly increased from less than 1 mg/L to ca. 200 mg/L as pH decreased from 12 to 10 and was consistent with the solubility [48] of calcium arsenite [As(III)]. This behavior seemed to suggest that arsenic was present as AsO_2^- in the leachates for pH between 10 and 12. At $\text{pH} < 10$, arsenic solubility was limited to the total arsenic content in the S/S As_2O_3 matrix.

3.2. Arsenic availability

Arsenic availability at pH 4.0 and 8.0 and arsenic availability at pH 7.0 with EDTA are compared in Fig. 5. In addition to availability results, total content and maximum solubility release reached using the solubility as a function of pH test method at $\text{pH} < 3$ are provided for comparison. When using the availability test method at pH 4.0 and 8.0, the availability of arsenic was found to be lower than the total contents (12 and 9% for the untreated As soil and the S/S treated As soil, respectively). For the EDTA extraction, arsenic availability was within the uncertainties of total content measurement. This difference in availability results is most likely due to operational differences between the test methods (i.e. use of a strong

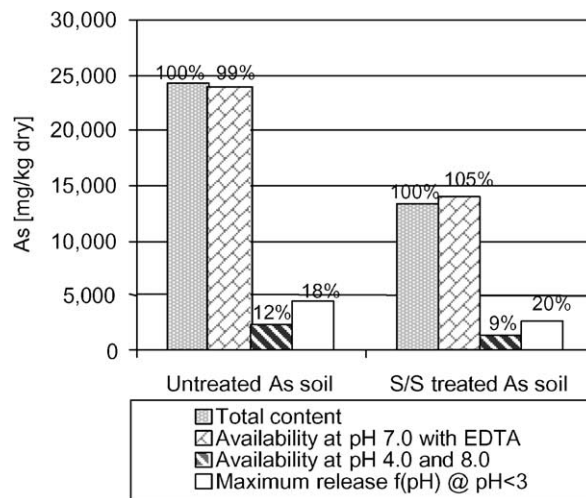


Fig. 5. Arsenic availability in the untreated As soil and S/S treated As soil compared to total arsenic contents.

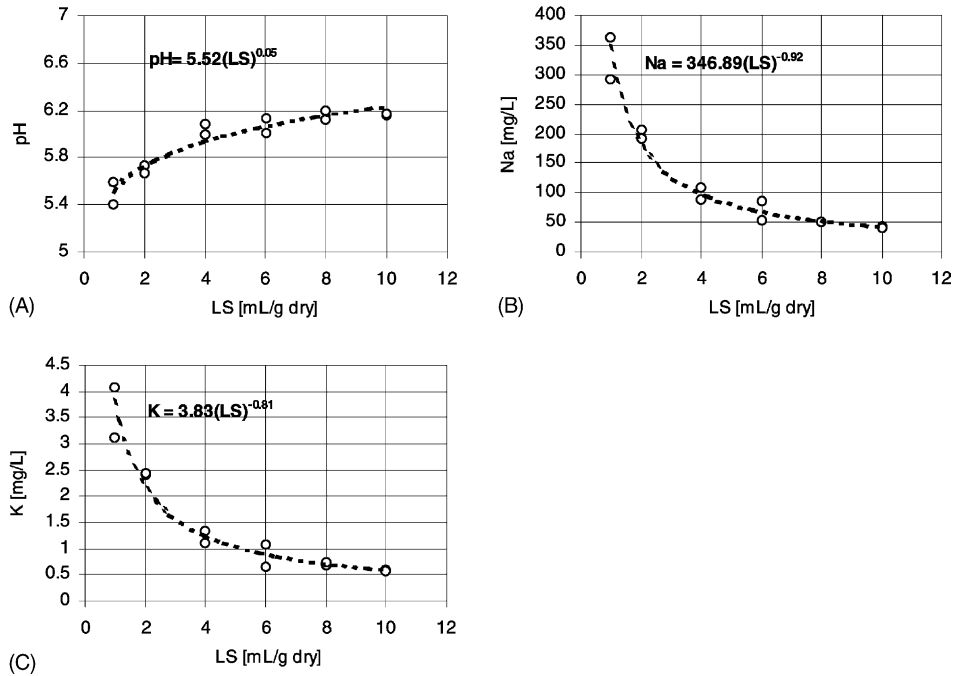


Fig. 6. Extractions at different low liquid–solid ratios—untreated As soil: (A) pH; (B) sodium and (C) potassium.

chelating agent in the availability at pH 7.0 with EDTA while use of nitric acid or potassium hydroxide in the availability at pH 4.0 and 8.0). In addition, comparison between arsenic availability at pH 4.0 and 8.0 and maximum release at pH <3 indicates that the availability of arsenic measured at pH 4.0 and 8.0 was most likely solubility limited which was not the case in the EDTA extraction.

3.3. Physical and chemical properties of the pore water of the matrices

Figs. 6 and 7 present the pH and concentrations of sodium and potassium as a function of the LS ratio for the untreated As soil and the S/S treated As soil. Table 2 provides a comparison of the physical and chemical properties measured for each test matrix and the estimated values for the pore water in each case. Available information was slightly different for each material because of the variations in methods and interpretation between the two laboratories. For the untreated As soil and the S/S treated As soil, charge balances on the pore water of the matrix indicated that anionic species other than OH^- (as obtained from pH measurement) were likely present in the matrix pore water. Therefore, the ionic strength was estimated assuming this species was monovalent (e.g. chloride). For the S/S As_2O_3 , chloride concentration at LS ratio of 2 mL/g was directly measured to be 1800 mg/L. In addition, the release of sodium and chloride at LS ratio of 2 mL/g corresponded to the total content added during the sample preparation (i.e. 1 wt.% NaCl) within analytical uncertainties.

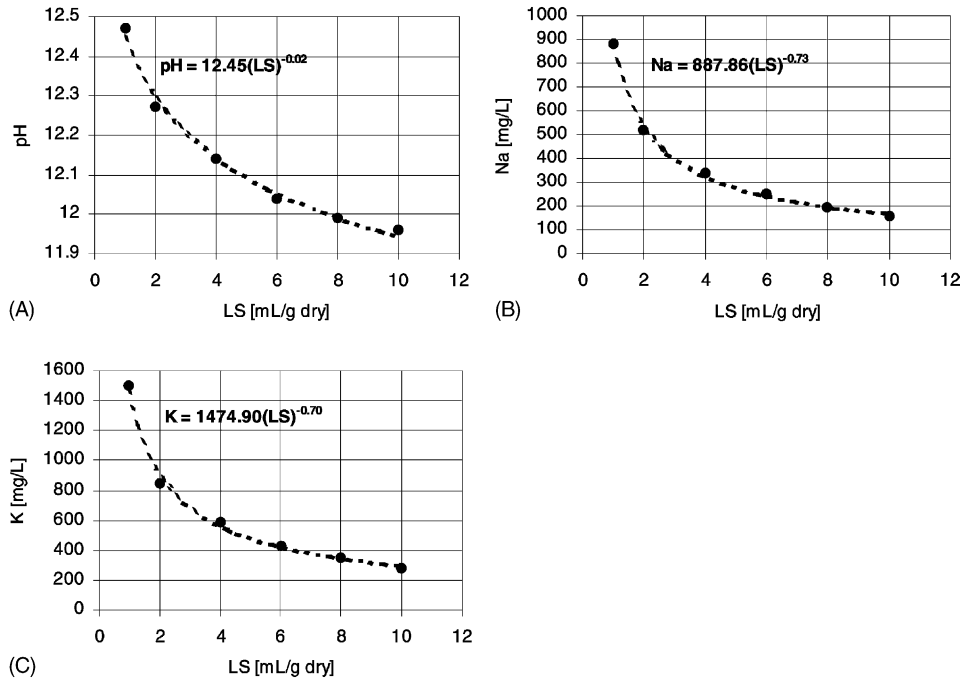


Fig. 7. Extractions at different low LS ratios—S/S treated As soil: (A) pH; (B) sodium and (C) potassium.

For S/S As_2O_3 , the total release of sodium, potassium and chloride was assumed constant and a mass balance was used to extrapolate from the concentrations at the lowest LS ratio experimentally measured to the estimated pore water LS ratio. Empirical curve fits were used to estimate the concentrations of sodium and potassium for the untreated As soil and the S/S treated As soil. pH was extrapolated for pore water estimation using an empirical curve fit for the untreated As soil and the S/S treated As soil, but assumed constant at 13.4 for the S/S As_2O_3 . The latter assumption was used because of incomplete data. Experimental results on arsenic oxidation state and speciation indicated in the literature [47] were used to suggest the predominant speciation of arsenic in the pore water. For the S/S As_2O_3 matrix, arsenic solubility seemed to have been controlled by the solubility of calcium arsenite in the pH range 10–12 and the predominant species of arsenic in the pore water of the S/S As_2O_3 matrix could have been AsO_2^- [48]. These results indicate the use of substantially different activities coefficients is necessary to evaluate diffusive mobility in pore water than would be estimated from extractions at LS ratio typical for most equilibrium batch tests (e.g. LS ratios of 5 or 10 mL/g).

3.4. Assessment of dynamic release: mass transfer leaching test

Final leachate pH of the untreated As soil obtained after each leaching interval (Fig. 8(A)) remained relatively constant around a pH value of ca. 6 which corresponds to the natural

Table 2
Physical properties of test matrices and chemical properties of leachates and pore water

Physical or chemical property	Test matrix		
	Untreated As soil	S/S treated As soil	S/S As ₂ O ₃ matrix
Moisture content (%)	21	18	6
Density (g/cm ³)	1.6	1.5	2.2
Open porosity (%) ^a	33	25	11
LS ratio estimated for p.w. (mL/g) ^b	0.3	0.2	0.06
pH (standard units)			
At LS 10 mL/g	6.2	12.0	na
At LS 2 mL/g	na ^c	na	13.4
At LS 1 mL/g	5.5	12.5	na
Estimated for p.w.	5.2	12.6	13.4 ^d
Na (mg/L)			
At LS 10 mL/g	50	100	na
At LS 2 mL/g	na	na	1,800
At LS 1 mL/g	400	900	na
Estimated for p.w.	1050	1130	62,100
K (mg/L)			
At LS 10 mL/g	0.5	300	na
At LS 2 mL/g	na	na	140
At LS 1 mL/g	4	1500	na
Estimated for p.w.	11	1930	4,680
Ionic strength (mol/L)			
At LS 5 mL/g	0.003	0.02	na
At LS 2 mL/g	na	na	0.25
Estimated for p.w.	0.05	0.09	3
Activity coefficient			
Charge ±1			
At LS 5 mL/g	0.94	0.88	na
At LS 2 mL/g	na	na	0.75
Estimated for p.w.	0.84	0.79	0.85
Charge ±2			
At LS 5 mL/g	0.80	0.62	na
At LS 2 mL/g	na	na	0.31
Estimated for p.w.	0.50	0.41	0.52
As speciation in p.w.	H ₂ AsO ₄ ⁻	H ₂ AsO ₄ ⁻	AsO ₂ ⁻

^a Porosity estimated from moisture content and matrix density for the untreated and S/S treated As soil; porosity measured by mercury intrusion analyses for the S/S As₂O₃ matrix.

^b p.w.: pore water.

^c na: not available.

^d Sufficient data was not available to extrapolate pH for this case, so the pH at LS ratio of 2 mL/g was assumed.

pH of the soil. For the S/S treated As soil and S/S As₂O₃, final leachate pH (Fig. 8(B)) was controlled by the release of hydroxides and the duration of the leaching period. Final leachate pHs were slightly greater for the S/S As₂O₃ than the ones obtained for the S/S treated As soil, which was consistent with the matrix buffering capacity. Mass and charge balances for

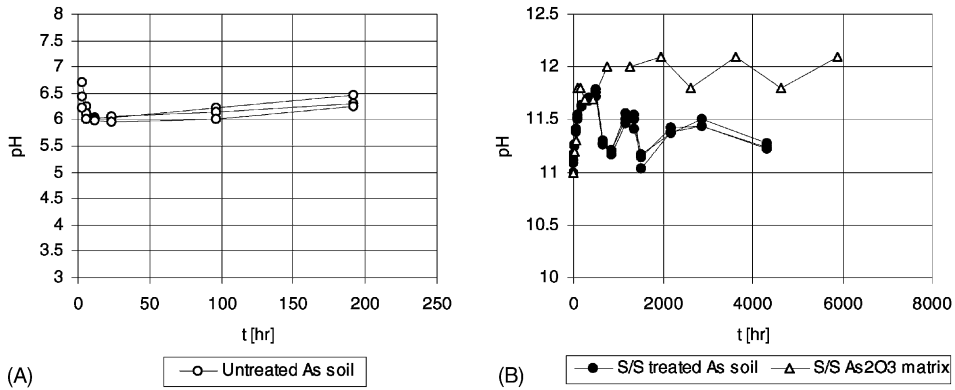


Fig. 8. Final leachate pH obtained after each leaching interval during mass transfer leaching test: (A) untreated As soil and (B) S/S treated As soil and S/S As₂O₃ matrix.

the leachates from the S/S treated As soil and S/S As₂O₃ showed that, for both matrices, the leachate pH was not controlled only by the release of calcium hydroxide, but also by the release of sodium hydroxide (Fig. 9(A) and (B), respectively) and probably potassium hydroxide, particularly during the initial leaching periods. However, for the S/S treated As soil, greater hydroxide concentrations were observed than indicated based on calcium and sodium concentrations during the last leaching periods, suggesting that reaction with atmospheric carbon dioxide infiltrating through leaching vessel seals might have occurred during testing.

Cumulative release of sodium from the three matrices is presented in Fig. 10. Cumulative release of chloride from the S/S As₂O₃ matrix is shown in Fig. 11. The release of sodium from the untreated As soil was very low with <0.1% released after 8 days of leaching, indicating significant sodium retention in the soil. For the S/S treated As soil, only ca. 50%

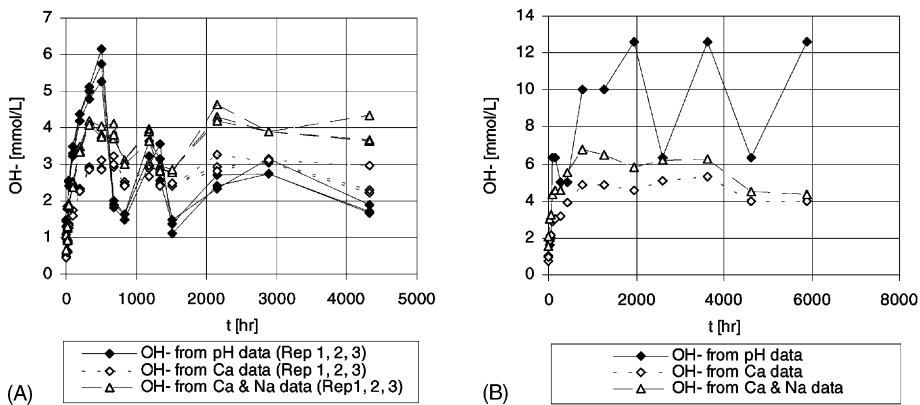


Fig. 9. Comparison of hydroxide concentration in the leachates as estimated from leachate pH, calcium concentration and calcium and sodium concentrations: (A) S/S treated As soil and (B) S/S As₂O₃ matrix.

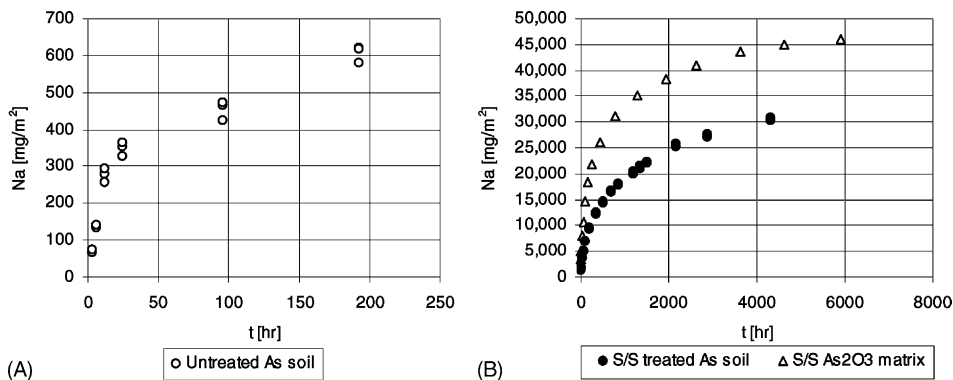


Fig. 10. Cumulative release of sodium during mass transfer leaching test with deionized water as a function of time from (A) the untreated As soil and (B) the S/S treated As soil and S/S As₂O₃ matrix.

of sodium from the untreated soil was released after 6 months of leaching with periodic renewals. For the S/S As₂O₃, a rapid release of sodium was observed with more than 80% of the sodium added during the sample preparation (i.e. 1% NaCl) released after 2 months of leaching. However, only 50% of the chloride added during the sample preparation was released after 8 months of leaching.

Cumulative release of calcium from the S/S treated As soil and S/S As₂O₃ is compared in Fig. 12(A). As with final leachate pH, the cumulative release of calcium from the S/S As₂O₃ matrix was slightly greater than observed from the S/S treated As soil, consistent with the matrix buffering capacity.

Cumulative release of arsenic from the three cases was: untreated As soil > S/S treated As soil > S/S As₂O₃ (Fig. 12(B)). This result was consistent with arsenic solubility and

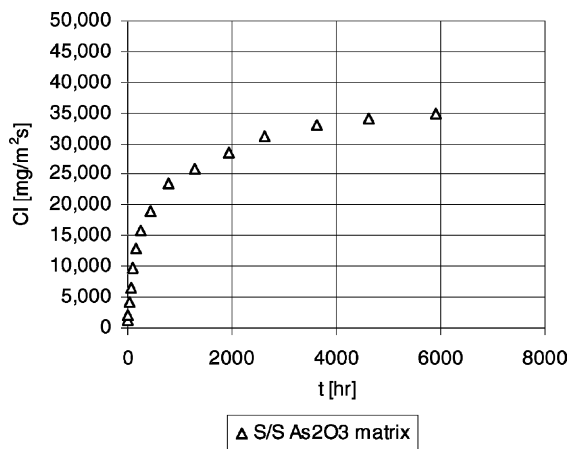


Fig. 11. Cumulative release of chloride during mass transfer leaching test with deionized water as a function of time from the S/S As₂O₃ matrix.

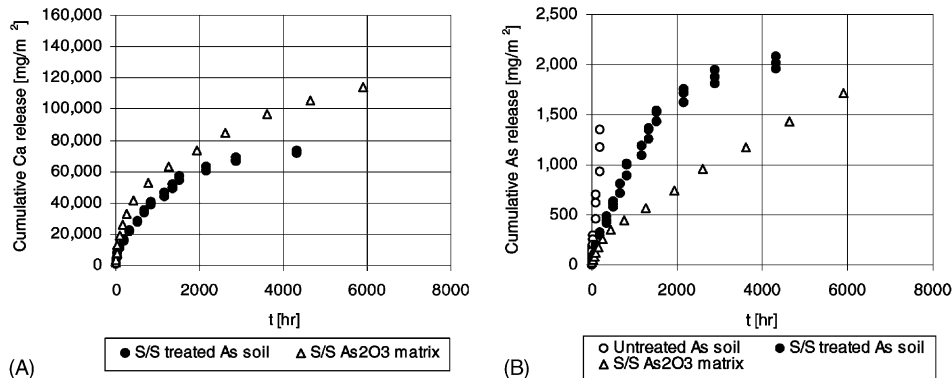


Fig. 12. Cumulative release as a function of time of (A) calcium and (B) arsenic during mass transfer leaching test with deionized water of the untreated As soil, S/S treated As soil and S/S As₂O₃ matrix.

final leachate pH. Indeed, at the natural pH of the soil, which also corresponds to the final leachate pH of the soil, the solubility of arsenic was ca. 60 mg/L while at the final leachate pH of the S/S treated As soil the solubility of arsenic was ca. 1 mg/L.

3.5. Assessment of dynamic release: release modeling

3.5.1. Leaching behavior of sodium and chloride: diffusion model

The one-dimensional diffusion model was used to describe the release of sodium from the untreated As soil. During the time scale of the laboratory testing (i.e. 8 days), no depletion of sodium within the matrix was observed. A three-dimensional diffusion model [12] was used to describe the release of sodium from the S/S treated As soil and S/S As₂O₃, as well as the release of chloride from the S/S As₂O₃. Use of a three-dimensional diffusion model for these cases was necessary because depletion of the species of concern was observed for both matrices during the time scale of the laboratory testing (i.e. 6 and 8 months, respectively). Estimates of observed diffusivity of sodium and chloride, assuming that all the total content in sodium and chloride was available for leaching, are provided in Table 3. The observed diffusivity of sodium in the untreated As soil was estimated from the log–log plot of the cumulative mass release as a function of time. Using the mass release data represented in this plot, an interval observed diffusivity was determined for each leaching interval where the slope of the plot was 0.5 ± 0.15 (apparent diffusion-controlled release) [49]. An estimated observed diffusivity was then calculated as an average of the interval observed diffusivity values. This method is presented in detail elsewhere [5]. For the solidified materials (S/S As soil and S/S As₂O₃ matrices), the observed diffusivities of sodium and chloride were estimated by simultaneous regression of the two parameters of the diffusion model (i.e. C_0 the initial leachable concentration and D_{obs} the observed diffusivity) [12,13]. Ratios of molecular diffusivity to observed diffusivity were compared to a tortuosity factor, τ , based on the Millington–Quirk tortuosity and matrix porosity. In all cases, the ratio of observed diffusivity to molecular diffusivity for sodium was significantly greater (up to three orders

Table 3
Parameter estimates from the diffusion model

	Sodium				Chloride			
	C_0 (kg/m ³)	D_{obs} ($\times 10^{12}$ m ² /s)	$D_{\text{m}}/D_{\text{obs}}^{\text{a}}$	τ^{b}	C_0 (kg/m ³)	D_{obs} ($\times 10^{12}$ m ² /s)	$D_{\text{m}}/D_{\text{obs}}^{\text{a}}$	τ^{b}
Untreated As soil ^c	7.5 ^d	0.3	4715	1.5	NA ^e	NA	NA	1.5
S/S treated As soil ^c	2.2 ^f	26.0 ^f	50.8	1.6	NA	NA	NA	1.6
S/S As ₂ O ₃ matrix	8.6 ^f	5.0 ^f	264	2.1	6.6 ^f	7.8 ^f	260	2.1

^a $D_{\text{m,Na}} = 1.32 \times 10^{-9}$ m²/s and $D_{\text{m,Cl}} = 2.03 \times 10^{-9}$ m²/s [41].

^b Estimated from Millington–Quirk tortuosity and matrix porosity, $\tau = \varepsilon \tau_{\text{MQ}} = \varepsilon \varepsilon^{-4/3} = \varepsilon^{-1/3}$. Porosity estimated from moisture content and matrix density for the untreated and S/S treated As soil (i.e. 33 and 25%, respectively); porosity measured by mercury intrusion analyses for the S/S As₂O₃ matrix (i.e. 11%).

^c Average of three replicates.

^d Total content in sodium.

^e NA: not applicable.

^f Regressed data using a three-dimensional diffusion model.

of magnitude) than the estimated tortuosity τ . This comparison indicates that significant chemical retention of sodium occurred either by cation exchange (as is likely the case for the low sodium content in a soil) or by other interactions with the cement matrix.

Comparison between experimental and simulated flux of sodium and chloride for both S/S matrices is presented in Figs. 13 and 14. The points represent the average experimental flux; the continuous or dashed curves represent the regressed simulation results. The three-dimensional diffusion model accurately represented the experimental data. Estimates of initial leachable concentration, C_0 , and observed diffusivity, D_{obs} , as simultaneously regressed to the diffusion model, are provided in Table 3. For the S/S treated As soil, the estimate of initial leachable concentration C_0 of sodium represented only ca. 50% of the

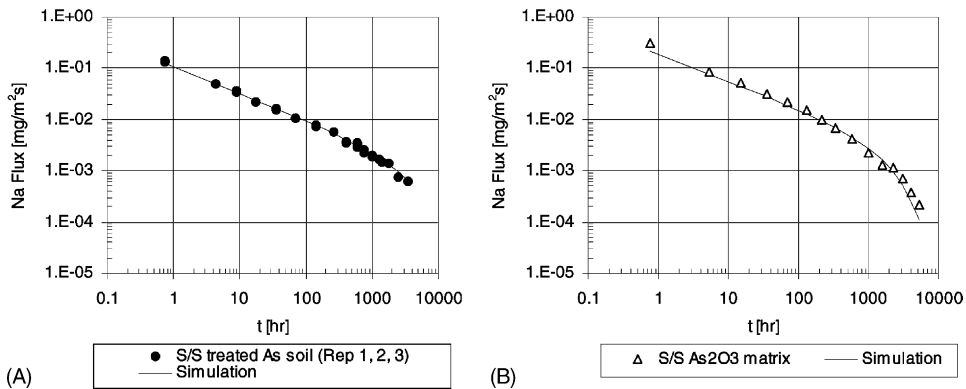


Fig. 13. Comparison of three-dimensional diffusion model and experimental data. Flux of sodium from the (A) S/S treated As soil and (B) S/S As₂O₃ matrix.

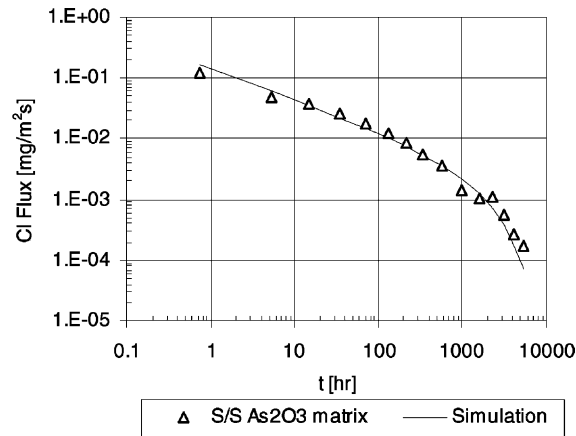


Fig. 14. Comparison of three-dimensional diffusion model and experimental data. Flux of chloride from the S/S As_2O_3 matrix.

sodium from the untreated soil. For the S/S As_2O_3 matrix, the estimate of C_0 for sodium represented 100% of the sodium added during the sample preparation, while the estimate of C_0 for chloride represented only 50%, indicating that part of the chloride added was stabilized within the S/S matrix by re-speciation with cement constituents.

3.5.2. Leaching behavior of calcium and arsenic: coupled dissolution–diffusion model

The predominant immobilization mechanism for arsenic in soil is largely considered to be by sorption to oxide minerals, especially iron oxide phases [49]. However, estimation of the iron oxide potentially available for sorption⁵ indicated arsenic saturation of oxide sorption sites in the presence of excess of arsenic. It is therefore reasonable to assume that a fraction of the arsenic was present as a precipitated solid in the soil pore water and that dissolution/precipitation was a controlling mechanism in the release of arsenic until precipitated arsenic was depleted. As precipitated arsenic is depleted, sorption of iron will be observed as an important contributor in retarding the release of arsenic. Since <0.06% of the total arsenic concentration was release after 8 days of leaching, adsorption/desorption of arsenic was not considered important for this analysis under these release conditions. However, the extent to which sorption mechanisms affect the transport of arsenic may be in the diffusivity term.

Under the above release assumptions, the release of arsenic from all three matrices was simulated using the coupled dissolution–diffusion model, which assumes precipitated solid phases within the pore structure. According to the experimental results obtained on the final leachate pH of the soil, no pH gradient within the soil matrix occurred during the leaching. In this case, the coupled dissolution–diffusion model is similar to a shrinking core model which implies that diffusion was the primary release mechanism for arsenic in this matrix

⁵ Assuming that all the iron was hydrous ferric oxide with a site concentration of 0.2 mol site/mol of iron, 0.13 mol site/kg of soil could potentially be available for sorption.

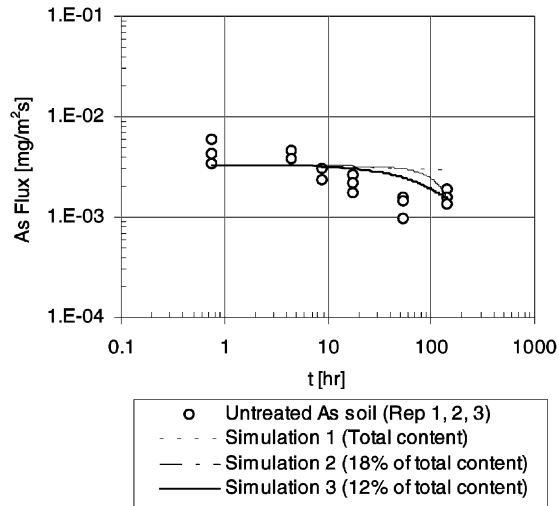


Fig. 15. Comparison of coupled dissolution–diffusion model and experimental data. Flux of arsenic from the untreated As soil.

with a driving force controlled by its solubility in the pore solution. Comparisons between the experimentally observed and simulated flux of arsenic are presented in Figs. 15–17. The points represent the average experimental flux; the continuous and dashed curves represent the regressed simulation results.

For the As untreated soil, simulation 1 was obtained assuming that all the total content in arsenic was available for leaching. Simulations 2 and 3 were obtained assuming that only ca. 18% (i.e. as found considering the maximum release at pH <3 from the release as a function of pH) and ca. 12% of the total content in arsenic (i.e. as found using availability at pH 4.0 and 8.0) were available for leaching, respectively. Only simulation 3 provided overall a good representation of the experimental leaching results, indicating that a significant fraction of arsenic was not available for leaching under the studied conditions. The differences in these simulation results illustrate the ambiguity of the availability term notion and the importance of selection of an appropriate initial solid phase concentration. In addition, the simulations indicated that no depletion of the arsenic solid phase at the matrix–leaching solution interface occurred during the initial 10 h of leaching, resulting in a simulated flux almost constant. As the arsenic solid phase became depleted at the matrix–leaching solution interface, the behavior of the simulated arsenic flux became consistent with that expected from a shrinking front type model.

For the S/S treated As soil, the solid phase concentration in arsenic was successively set to the total content in arsenic (i.e. simulation 1) and fractions of the total content (i.e. ca. 20% (simulation 2) of the total content as found considering the maximum release at pH <3 from the release as a function of pH and ca. 9% (simulation 3) of the total content as found using availability at pH 4.0 and 8.0). For the S/S As₂O₃ matrix, the solid phase concentration in arsenic was set to the total content in arsenic. Simulation results were not as sensitive to this parameter for the S/S matrices but were sensitive to the evolution of hydroxide release.

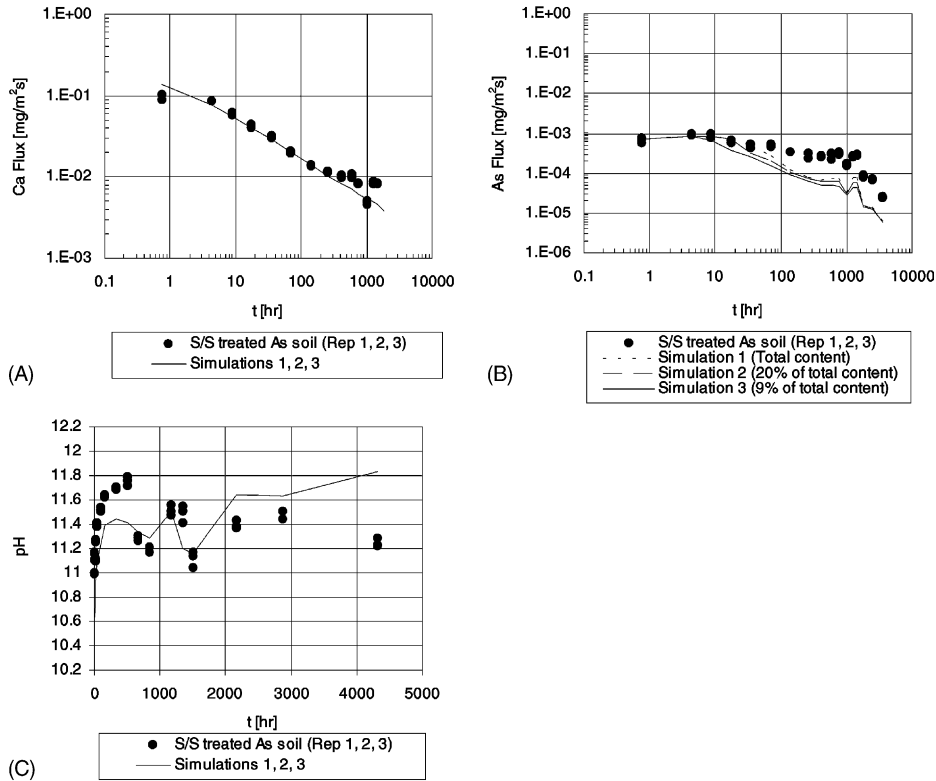


Fig. 16. Comparison of coupled dissolution–diffusion model and experimental data: (A) flux of calcium; (B) flux of arsenic and (C) final leachate pH. S/S treated As soil.

In the model, the solution (leachate pH) is controlled by the release of matrix constituents (i.e. $\text{Ca}(\text{OH})_2$) into a finite bath. Thus, the simulated solution pH responds dynamically to accumulation of release species in the leachate and time intervals. The model predicted lower pH values during the initial leaching periods than the ones experimentally observed. This is a consequence of the release of sodium and potassium hydroxides during the first leaching periods that are not accounted for by the model. The simulations of the pH profile generated during leaching within the matrix and of the leachate pH were based on the hydroxide provided only by the release of calcium hydroxide. Lower predicted pH values resulted in higher predicted arsenic solubility. This effect may explain the differences between the experimental results and the simulation results observed during the initial six leaching periods for both the S/S treated As soil and the S/S As_2O_3 matrix. In addition, for the S/S treated As soil, during the last three leaching periods, the model predicted higher pH values than the ones experimentally observed, leading to lower predicted arsenic solubility.

Values of the regressed parameters used for the simulations are provided in Table 4. These values were initially set to experimental data. Simulation results were fitted to experimental results by regressing the activity coefficient and then the effective diffusivities, until the

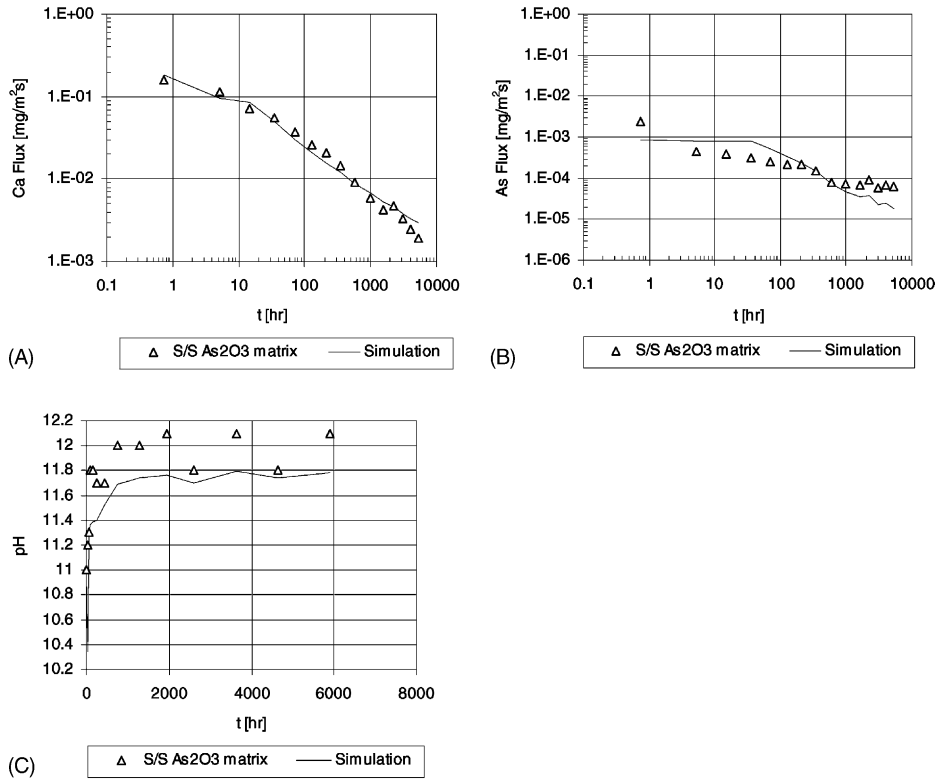


Fig. 17. Comparison of coupled dissolution–diffusion model and experimental data: (A) flux of calcium; (B) flux of arsenic and (C) final leachate pH. S/S As₂O₃ matrix.

model provided the best fit. The regression equations of the solubility of arsenic as a function of pH were obtained from the results of the test solubility and release as a function of pH. As these equations apply to conditions where the activity coefficient is equal to one, modification to a different ionic strength using the estimated activity coefficient was done.⁶ Ratios of the molecular diffusivity to the observed diffusivity were compared to a tortuosity factor estimated from the Millington–Quirk tortuosity and matrix porosity (i.e. $\tau = \varepsilon\tau_{MQ} = \varepsilon\varepsilon^{-4/3} = \varepsilon^{-1/3}$, where τ_{MQ} is the Millington–Quirk tortuosity and ε is the matrix porosity). For all cases, the regressed values of the activity coefficient were greater than the value estimated based on experimental data (Table 4). For the untreated As soil, the ratio of the regressed effective diffusivity to molecular diffusivity of arsenic was ca. 20 times greater than the estimated matrix tortuosity, suggesting that ion exchange of arsenic in the soil may have been a contributor to overall arsenic retention. However, the similarity between these two estimates for both S/S matrices suggests that arsenic solubility in the pore water was

⁶ Species activity coefficient was assumed constant over the entire pH range. This is one limitation of the current approach, which has been further examined and adjusted in the model [29].

Table 4
Parameters values from the coupled dissolution–diffusion model

	Untreated As soil	S/S treated As soil	S/S As ₂ O ₃ matrix
Porosity (%)	33	25	11
Solid phases (kg/m ³ of porous matrix)			
Ca(OH) ₂	Na ^a	16	230
As	30.70 (Simulation 1) 5.50 (Simulation 2) 3.70 (Simulation 3)	9.60 (Simulation 1) 1.90 (Simulation 2) 0.90 (Simulation 3)	16.6
Arsenic solubility	Experimental data ^b	Experimental data ^c	Experimental data ^d
Activity coefficient	0.80	0.50	0.80
Effective diffusivity, D_e ($\times 10^{10}$ m ² /s)			
Ca	NA	2	0.60
As	0.40	4	2
S.E. ^e			
Ca	NA	0.11	0.05
As	0.11 (Simulation 1) 0.09 (Simulation 2) 0.07 (Simulation 3)	0.16 (Simulation 1) 0.19 (Simulation 2) 0.21 (Simulation 3)	0.10
τ^f	1.5	1.6	2.1
D_m/D_e			
Ca	NA	4.0 ^g	13.2 ^g
As	29 ^h	2.5 ⁱ	7.0 ^j

^a NA: not applicable.

^b Use of the experimental solubility data obtained at the natural pH of the untreated As soil (i.e. 60 mg/L).

^c Use of the equation regressed from the experimental solubility data obtained on the S/S treated As soil. For pH > 7, this equation is: $\log(\text{As solubility}) (\text{mol/L}) = 0.025\text{pH}^3 - 0.752\text{pH}^2 + 7.073\text{pH} - 25.053$.

^d Use of the equation regressed from the experimental solubility data obtained on the S/S As₂O₃ matrix. For pH > 11, this equation is: $\log(\text{As solubility}) (\text{mol/L}) = 0.25\text{pH}^3 - 7.73\text{pH}^2 + 78.72\text{pH} - 261.50$.

^e Standard error.

^f Estimated from Millington–Quirk tortuosity and matrix porosity, $\tau = \varepsilon \tau_{\text{MQ}} = \varepsilon \varepsilon^{-4/3} = \varepsilon^{-1/3}$.

^g $D_{m,\text{Ca}} = 7.92 \times 10^{-10}$ m²/s [41].

^h $D_{m,\text{H}_2\text{AsO}_4^-} = 11.30 \times 10^{-10}$ m²/s [42].

ⁱ $D_{m,\text{HAsO}_4^{2-}} = 9.96 \times 10^{-10}$ m²/s [42].

^j $D_{m,\text{AsO}_2^-} = 14.00 \times 10^{-10}$ m²/s [42].

controlling release for these cases. In addition, the difference between these two estimates may be attributable, in part, to changes in matrix porosity that results from leaching but has been assumed constant in the model.

The coupled dissolution–diffusion model was used to estimate the depths of the moving fronts of calcium and arsenic in the S/S matrices over the duration of laboratory testing (i.e. 6 months for the S/S treated As soil and 8 months for the S/S As₂O₃ matrix). Moving fronts of calcium of ca. 8.9 mm and 1.0 mm were estimated for the S/S treated As soil and the S/S As₂O₃ matrix, respectively. The model indicated that if the total content in arsenic was available (i.e. simulation 1), after 6 months of leaching, the depletion of arsenic within the S/S treated As soil would have occurred up to a depth of ca. 125 μm from the

surface. When considering that only ca. 20% of the total content in arsenic was available for leaching (simulation 2), the depth of depletion was 415 μm and when considering that ca. 9% was available (simulation 3), the depth of depletion was 790 μm . These results showed that the depth of depletion depends greatly on the solid phase concentration used during the simulation. For the S/S As_2O_3 matrix, the model indicated that the depletion of arsenic had occurred up to a depth of ca. 180 μm after 8 months of leaching. These theoretical depths of arsenic depletion within both matrices indicated that the moving front of arsenic was, in both cases, near the interface between the matrix and the leaching solution. Therefore, during the time scale of laboratory testing, the release of arsenic was mainly controlled for both matrices by solubilization at the solid–liquid interface (i.e. at the interface between the matrix and the leaching solution) followed by a moving front.

4. Conclusions

Integrated use of equilibrium and mass transfer rate leach tests in conjunction with appropriate mass transfer models can provide a useful framework for evaluating leaching of inorganic contaminants from soils and cement-based matrices. The solubility of specific species as a function of pH can be determined using equilibrium-based leaching tests and then used for parameterization of the coupled dissolution–diffusion model. However, the solubility measured must be corrected for the ionic strength present in the pore solution. Activity coefficients for the pore solution can be estimated using low LS ratio equilibrium extractions and determination of the resulting ionic strength.

The coupled dissolution–diffusion model effectively reflected the main phenomena involved in the mass transfer during the time scale of the laboratory testing (i.e. 8 days for the untreated As soil, 6 months for the S/S treated As soil and 8 months for the As_2O_3 S/S matrix). Simulation results obtained using the coupled dissolution–diffusion model showed that, on the time scale of laboratory testing: (i) the release of arsenic from the soil matrix was governed by diffusion with a driving force controlled by the solubility of arsenic in the pore solution, and (ii) the release of arsenic from the cement-based matrices was mainly controlled by solubilization at the solid–liquid interface (i.e. at the interface between the matrix and the leaching solution), followed by a moving front. However, ion exchange phenomena, in addition to pore water solubility, may have significantly impacted the release rates from soil for the species of concern. Simulation results also showed that inaccurate estimates of contaminant solid phase concentration available for leaching (i.e. total content versus available content) can result in inaccurate representation of the factors controlling release (i.e. solubilization phenomenon versus moving front) and therefore can result in significant errors in long-term release estimates.

Acknowledgements

This research was supported by the Hazardous Substance Management Research Center (HSMRC), USA, an Advanced Technology Center of the New Jersey Commission on

Science and Technology and the Association RE.CO.R.D. (Waste Research Cooperative Network, France).

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