# Kinetic Mass Transfer Model for Contaminant Migration in Soils

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**Abstract.** This work studied the transport phenomena in the soil of the Gramacho MSW landfill located in Rio de Janeiro, Brazil. A model was proposed to determine the mass transfer rate of the leachate contaminant ions to the soil particles. Previous researchers have focused on the diffusion and sorption phenomena using simple relations that do not completely explain the data of overall mass transfer obtained by laboratory experiments. Thus, this work proposes a modified rate equation implemented into MPHMTP software that takes into account the combined mechanisms of advection and diffusion in the leachate and sorption at the particle surface followed by diffusion in the interior of the soil particle. The model predictions were compared with laboratory-measured data and presented better agreement compared to those obtained using the commercial POLLUTE software.

Keywords: diffusion, sorption, chemical kinetic, leachate, landfill, mass transfer.

# 1. Introduction

In Brazil, the system of management for urban solid residue uses the landfill as an economically suitable solution for the final solid waste disposal. Landfill leachate is produced by the degradation of waste and the movement of rainwater that occurs within disposed layers. When it is drained from the landfill, the leachate contains dissolved and suspended materials that interact with soil particles, depending on the soil physical and chemical characteristics. The leachate properties vary depending on the waste and the age of the landfill, which makes it difficult to treat because it may contain many chemical compounds that, under the influence of natural agents (rain and microorganisms), generate contaminants that are difficult to mitigate.

According to some authors (Bear, 1972; Gelhar, 1993; Domenico & Schwartz, 1998; Fetter, 1999), the groundwater transport of contaminants has been one of the most important research topics in hydrology and engineering in the recent decades. Such studies aimed to find methodologies able to reduce possible social and ecological impacts due to waste disposal. To date, the fate of contaminants into soil is still receiving considerable attention due to the impact on several ecosystems.

The migration of contaminant ions into the soil is influenced by several processes that can be physical (advection and hydrodynamic dispersion), chemical (sorption, complexation and precipitation) and biological (degradation by biotic or abiotic factors). Several researchers have addressed the contamination phenomenon by different techniques (Goodall & Quigley, 1977, Rowe, 1988, Barone *et al.*, 1989, Schakelford & Daniel, 1991, Mitchell, 1994, Ehrlich *et al.*, 1994, Barbosa *et al.*, 1996, Boscov *et al.*, 1999, Leite & Paraguassu, 2002, Azevedo *et al.*, 2003). Mostly, the focus of these studies has been the pollutant transport mechanisms through artificial barriers or natural soil with the aims of elucidating the complex phenomena and developing new technologies to mitigate or minimize environmental impacts.

The study of contaminant transport into the soil has, so far, been carried out based on the assumption that hydraulic conductivity is the main phenomenon responsible for the infiltration of the contaminant. However, experimental investigations have evidenced that the molecular diffusion process is a significant transport mechanism and, for practical applications, cannot be neglected (Crooks & Quigley, 1984, Quigley et al., 1987, Johnson et al., 1989). Depending on the contaminant species, the chemical process may be relevant, and complex chemical reactions will take place. To take into consideration and identify the relevant phenomena coupled with fluid flow and mass transfer, comprehensive mathematical models have been developed. However, most of the models treat individual and simplified phenomena (Liu et al., 2000). Therefore, mathematical formulations that consider complex transport mechanisms and chemical kinetics (Ehrlich and Ribeiro, 1995) have yet to be developed. In this paper a mathematical model to pre-

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dict the mass transport within the landfill soil is proposed and validated with experimental data.

Studies carried out on the soil and leachate of the Gramacho Municipal solid waste (MSW) located at Duque de Caxias city, Rio de Janeiro State, Brazil, have considered only the mechanisms of sorption and diffusion of ions from leachate to the soil and vice versa (Barbosa, 1994; Ritter, 1998, Ritter *et al.*, 1999, Ritter & Campos, 2006). The experimental data from diffusion tests with non-reactive chloride and sodium ions and reactive potassium and ammonium ions have shown a good fit with the POLLUTE software (Rowe & Booker, 1994), which bases the calculations on isothermal sorption theory. In contrast, experiments carried out with calcium ion have not yielded a good fit, indicating that these mechanisms are not the predominant ones.

This research focuses on the transport process and aims to predict the kinetics of mass transfer in a landfill soil (Araújo, 2006). It is expected that phenomenological models will better reproduce the behavior of contaminants in these environments. A software termed MPHMTP (Multi Phase Heat and Mass Transfer Program), developed by Castro (2000), was used in this study. The software allows the implementation of transport equations of contaminants in the soil, taking into consideration the coupled mass transfer phenomena (advection, diffusion, sorption and chemical reactions).

The model proposed in this work was applied to the experimental data obtained by Ritter & Gatto (2003) and compared with simulation results presented by Pinto (2004).

# 2. Experimental Data

#### 2.1. Experimental program history

The Gramacho Metropolitan Landfill occupies an area of 1.2 km<sup>2</sup> and is situated in a region of mangroves on the shores of the Guanabara Bay, close to the Sarapuí and Iguaçu rivers, over an organo-saline clay deposit, permanently submerged. The Gramacho MSW has been under recuperation since 1996, and several remediation actions to avoid contamination have been implemented. These actions are mainly a lateral channel that receives the leachate and a lateral trench, filled with the local organic clay, in the perimeter of the landfill, to compose a leachate collection system (Ritter & Campos, 2006). The trench was excavated very deeply to reach the local foundation organic clay. Tables 1 and 2 show, respectively, the experimentally determined parameters for the soil and leachate from the landfill (Barbosa, 1994, Ritter *et al*, 2004).

Previous studies emphasized the importance of salinity on the transport of contaminants through the landfill foundation (Barbosa, 1994 and Barbosa *et al.* 1996). It was identified by diffusion experiments with leachate that the leachate establishes a flow of chemical species in both di-

Fraction < 5 $\mu$ m (%)	70
Moisture content (%)	140 a 170
Liquid limit (%)	167
Plasticity limit (%)	77
Porosity	~0.70 a 0.80
Density of grains	2.41
Plasticity index (PI) (%)	90

Table 2 - Chemical composition of the leachate and pore water.

Chemical analysis	Leachate	Pore water
pH	7.9	8.26
Conductivity (mS.cm <sup>-1</sup> )	24.4	22.1
$Cl^{-1}(mg.L^{-1})$	4367	6105
$Na^{+}$ (mg.L <sup>-1</sup> )	3089	4475
$K^{+}$ (mg.L <sup>-1</sup> )	1681	543
$\mathrm{NH}_{4}^{+}$ (mg/L)	1815	92
$\operatorname{Ca}^{+2}(\operatorname{mg/L})$	203	365
$Mg^{+2}$ (mg/L)	92	850

rections (for the soil leachate and vice versa). Chloride, sodium, calcium and magnesium diffuse from soil to leachate because these ions have high concentrations in the saline organic soil (see Table 2); conversely, potassium has a higher concentration in the leachate compared to landfill soil. Barbosa (1994) evaluated the diffusion process in the soil of Gramacho's landfill using the software POLLUTE, where the effective diffusion coefficients of most important ions were estimated. It was verified that the Cl<sup>-</sup> and SO<sub>4</sub><sup>2</sup></sup> anions can be considered conservative species. The results for Na<sup>+</sup> and Mg<sup>2+</sup>, assuming no sorption for these ions, agreed well with experimental data obtained in sorption and diffusion experiments carried on a laboratory scale. For  $K^{+}$  and  $Ca^{2+}$ , using Pollute software, the model predictions showed large divergence from experimental ones, indicating that sorption theory may not be applicable to predict the migration of these ions.

## 3. Model Formulation

In a multiphase flow, the chemical species are mixed, and thus, it is possible to describe the presence of each ion by its molar or mass fractions. A general transport equation that takes into account the contaminant concentration within the soil and leachate is presented by Eq. (1):

$$\frac{\partial(\rho_i \varepsilon_i \phi_k)}{\partial t} + \frac{\partial}{\partial x_j} (\rho_i \varepsilon_i u_j \phi_k) = \frac{\partial}{\partial x_j} \left( \Gamma_{\phi_k} \frac{\partial \phi_k}{\partial x_j} \right) + S_{\phi_k}$$
(1)

The indexes *i* and *k* represent the phases and chemical species, respectively, while *j* indicates the spatial coordinates.  $\rho$  and *u* are the phase density and velocity components, respectively.  $\Gamma$  is the effective ion diffusion into the phase.  $\phi_k$  is the mass fraction of the species,  $\varepsilon_i$  is the phase volume fraction of each phase, *t* is time and *x* is the spatial coordinate. A typical control volume showing the coexistence of both phases, solid and interstitial liquid, with their respective ions is schematically presented in Fig. 1a.

Equation (1) represents the mass conservation for each of the ions present in an individual phase, solid or liquid. The first term on the left side of the equation is the mass fraction accumulation rate, while the second one is the convective contribution due to phase motion. The first term on the right side is the contribution due to ion diffusion.  $S_{\phi_k}$  is the so-called source or sink term, which accounts for ion exchange due to chemical and physical phenomena at the phase interfaces or within the phase by neutralization or chemical reactions. In this investigation, the source term is used to calculate the mass transfer from solid to liquid phases and vice-versa, including sorption, desorption and all other solid-liquid ion interactions.

To establish a consistent model of the ion transport in both phases, this investigation assumed that local equilibrium holds at the interfaces of solid and liquid leachate, and therefore, the ion exchange can be modeled by considering three distinct resistance steps to the mass transfer as follows: 1) transport of the contaminant in the liquid phase to the surface of the particle (advection, diffusion and dispersion), 2) sorption / desorption of the contaminant at the surface of the solid particle and 3) diffusion of the contaminant inside the particle of soil These three mechanisms are schematically shown in Fig. 1b, which represents an amplified view of the particle surface and the interactions of ions belonging to the solid particle and the interstitial liquid. As depicted in the Fig. 1b, the equilibrium concentrations of the ions in the particle and in the liquid boundary layer are not the same due to internal and external interactions. There exists a concentration gradient in the liquid phase, which forms a boundary layer, while another internal gradient is established in the vicinity of the particle surface. In the interior of the particle there are ions and compounds with the ability to attach or react with the contaminants and absorb them permanently or vice-versa. These phenomena can occur by physical or chemical affinity. To construct a model capable of quantifying these mass and ion transfers, it is important to image the equilibrium profiles of the contaminant concentration in the system and formulate transport resistances for each of these phenomena. Inside of the particles, the stationary diffusive phenomenon is predominant due to the concentration gradient imposed by near-surface interactions, and the parameter that controls this inner diffusion can be obtained by batch test equilibrium experiments, which characterize the particular system as solidliquid. On the surface, which is in contact with the contaminant, advection and diffusion simultaneously occur, forming hydrodynamic and concentration boundary layers. At the interface, the sorption phenomenon occurs in the active sites. The solid particle geometry obviously affects the values of equilibrium concentrations in the solid liquid system.

To account for these phenomena, a rate equation that is able to account for the simultaneous resistance of the boundary layers and differences in the ion equilibria at the particle surface is presented in Eq. (2). According to this formulation, the source term can be modeled by introducing a coefficient or specific rate of transfer,  $\beta_p$ , which represents the specific rate proportional to the equilibrium driving force for ion transfer. This formulation is general and can represent several transport resistances, depending on the mass transfer coefficient formulation. In this investi-



Figure 1 - Mechanism for the formulation of the kinetics of mass transfer of ions between the leachate and soil.

gation a kinetic rate constant is introduced to account for the mass transfer resistance at the particle surface and chemical control. This is equivalent to the linear sorption isotherm when the exponent of the driving concentration is unitary and the equilibrium concentration at the interface is constant. Thus, it is possible to consider a general isotherm formulation. Therefore, in this model, the general rate equation for mass transfer is proposed, as follows:

$$S_{\phi_k} = k_{\phi_k} \beta_{\phi_k} A_{s-l} [\rho_l \varepsilon_l] [\phi_k - \phi_k^*]^n$$
<sup>(2)</sup>

where  $k_{\phi_k}$  is the kinetic constant for the transfer of k ion,  $A_{s,l}$  is the interfacial area between solid and liquid,  $\beta_{\phi_k}$  is the effective mass transfer coefficient of the k ion and  $\phi_k$  is the interface equilibrium concentration of the k ion. The exponent coefficient in Eq. (2) represents a generalization for the description of the equilibrium behavior at the interface; in the particular case where n = 1 it will represent the classical formulation for the linear sorption rate. These parameters can be numerically optimized to reproduce the experimental data and thus can be used to predict temporal and spatial contamination profiles. The contact between solid particles and interstitial liquid and the effective mass transfer coefficient can be determined by Eqs. (3) and (4):

$$A_{s-l} = \frac{6\varepsilon_s}{d_s \phi_s} \tag{3}$$

$$\beta_{\phi_k} = \frac{ShD_{\phi_k}^l}{d_s \phi_s} \tag{4}$$

in which, Sh, the Sherwood number, is given by

$$Sh = 1.17(R_e)^{0.585} (Sc_{\phi_e})^{1/3}$$
(5)

with Reynolds and Schmidt numbers given by Eqs. (6) and (7),

$$R_e = \frac{\rho_l \varepsilon_l |\vec{U}_l - \vec{U}_s| (d_s \phi_s)}{\mu_l}$$
(6)

$$Sc_{\phi_k} = \frac{\mu_l}{\rho_l D_{\phi_k}^l} \tag{7}$$

The variables and symbols used in the above equations are listed in Table 3.

#### 3.1. MPHMTP Software

The software (MPHMTP – Multi Phase Heat and Mass Transfer Program) was developed by Castro (2000), coded in Fortran 90/95. The software uses different module interfaces for input data, geometry construction, phase properties, boundary, initial condition settings and output data customizations. The rate transfer equations are implemented into a specific module with flexibility for user supply expression for rate transfer depending on the ion considered. The user interfaces are subroutines that must be implemented and customized by the user. The software

Table 3 - Variables and symbols used in the above equations.

Variables	Units	
ε <sub>s</sub>		Solid phase volumetric fraction
ε		Liquid phase volumetric fraction
ds	m	Soil particles average diameter
φs		Soil particles form factor
$\beta_{\phi_k}$	m.s <sup>-1</sup>	Mass transfer coefficient
$D^l_{\phi_k}$	m <sup>2</sup> .year <sup>-1</sup>	Chemical species diffusion coefficient <i>i</i> , in the liquid phase
$R_{_{e}}$		Reynolds number changed between the liquid and solid phases
$Sc_{\phi_k}$		Schmidt number
$\rho_l$	kg.m <sup>-3</sup>	Liquid phase density
$U_{_{I}}$	m.s <sup>-1</sup>	Velocity in the liquid phase
$U_{_s}$	$m.s^{-1}$	Velocity in the solid phase
μ	Pa.s	Liquid phase viscosity

solves the complete transport equation for a generic species or ion, and the transfer coefficients together with the source terms are calculated interactively by an external subroutine furnished by the user. The numerical solution is based on the Finite Volume Method (FVM), and the time integration is based on the fully implicit formulation (Patankar, 1985). The solution is obtained for a generalized coordinate system, which allows perfect adjustment of the calculation domain to complex geometries of the soil layers in the landfill. The discrete algebraic equations are solved using the ADI-TDMA algorithm (Alternate Direction Iteration Tri-Diagonal Matrix algorithm). The properties and source term definitions subroutine allows the user to consider every kind of media, such as non-uniform soil or different configurations of soils layers with different properties. In the source term module, the user can add new routines to calculate the local mass transfer rates of each control volume within the domain.

## 4. Results and Discussions

As discussed in the model features, experimental data were used to determine the model parameters accounting for the mass transfer phenomena. Two laboratory scale experiments were performed: the equilibrium batch tests and diffusion tests. The equilibrium experiments were used to determine the equilibrium concentration of each soil-leachate system. Using the MPHMTP software, the input parameters obtained from laboratory diffusion tests, the geometry of the experimental apparatus and the initial conditions, the simulations were carried out for each ion to obtain the best fit for the model parameters. Table 4 presents the results of the equilibrium tests and model parameters determined in this study. The results presented in Table 4 were obtained by iterative refinement until the numerical

 Table 4 - Best fitting of model parameters obtained by numerical simulations.

Ion	k	$\phi_k^*$ (mg/L)	n	$D_e$ (m <sup>2</sup> /year)
Cl	2*10-6	5372.4	1.05	0.064
$Na^+$	3*10-9	5012.0	1.50	0.035
$Ca^{+2}$	9.58*10-8	332.15	1.54 / 1.51	0.025
$Mg^{+2}$	8*10-6	467.5	2.00	0.086
$\mathbf{K}^{*}$	1.05*10-5	434.4	1.32	0.062
$\mathrm{NH}_{4}^{+}$	2.50*10 <sup>-2</sup>	754.4	1.75	0.062

and experimental results showed close agreement, with the exception of  $D_e$ , which assumed the values of  $D_0$  for a free dilute solution in water (Lerman, 1979). Therefore, in this model effective diffusion coefficients were not used; on the contrary, all the effects of ions interactions with the media were regarded as source terms. This was done due to the ability of the model to deal with specific phenomena. This approach has the advantage of quantifying the separate process. In the numerical procedure, the criterion used to stop the calculations was the lowest global error for all species considered. The experiments were carried out for 72 h for diffusion cells and 48 h for bath equilibrium experiments. The model was used to reproduce the whole experimental procedure, and the final concentrations were compared for each ion prediction.

The model predictions were divided into reactive and non-reactive ones. The non-reactive ions can be accurately predicted by linear sorption isotherms, while the reactive ones usually present a complex behavior. This model was intended to show that both behaviors can be accurately predicted by this formulation.

#### 4.1. Non-reactive ions

Figures 2a and 2b show the profiles of ion diffusion in the experimental Barone cell for Cl<sup>-</sup> and Na<sup>+</sup>, regarded as non-reactive ions for comparisons with experimental data and previous models used in POLLUTE software and sorption isotherms. In these figures are also shown the reference concentration values for soil and leachate that are assumed as initial conditions for the calculations. The POLLUTE software can predict only the soil domain; in contrast, the MPHMTP considers both connected domains, the soil and reservoir, and does not need to impose boundary conditions on the soil reservoir interface, as required by POLLUTE. This software feature avoids additional assumptions regarding the surface boundary conditions. Although in the case of non-reactive ions the formulations for both software are essentially the same, due to the more realistic treatment of the interface between soil and reservoir, the MPHMTP presents closer agreement with the experimental data considering both formulations, sorption isotherms (UFF sorption model) and present formulation (UFF kinetic model). Inside of the reservoir, the diffusion of ions occurs in free solution, and the ion concentration profile is determined by the diffusion into the liquid phase until the equilibrium condition is achieved at the soil reservoir interface. Although the liquid concentration gradients were not measured, the present model seemed to better reproduce the liquid concentration profile and did not present discontinuity in the interstitial liquid concentrations at the soil reservoir interface. For the chloride ion, the value of the effective diffusion coefficient  $(D_i)$  was assumed to be equal the diffusion coefficient in free solution  $(D_0)$  for ions in aqueous solution at 25 °C, according to the literature (0.064 m<sup>2</sup>/year). In this



Figure 2 - Profile of molecular diffusion for chloride ions (a) and sodium (b) using the experimental results of 2003 (duration of test 72 h).

study the diffusion coefficient for sodium ions assumed the value of  $0.035 \text{ m}^2$ /year.

Figures 3 (a) and (b) show the comparison for model predictions and experimental data for the Ca<sup>2+</sup> and Mg<sup>2+</sup> ions. For both ions, the present model showed closer agreement with experimental measurements. The experimental measurements for Ca<sup>2+</sup> showed an atypical behavior that cannot be represented by sorption isotherms and distribution coefficients,  $k_a$ , because the intrinsic solution for these models does not allows signal changes in the derivative of the concentration curves. This atypical behavior can only be traced by a kinetic model, as presented in this study. For the Mg<sup>2+</sup> ion, all models presented the same pattern; however, the present model was able to get closer to the experimental results. An excellent agreement was obtained with the kinetic model, which is credited to its ability to consider local changes in the mass transfer rates depending upon local non-equilibrium conditions, which is not possible by constant effective diffusion coefficients formulations or retardations terms, as considered in the partition coefficients formulations such as  $k_{a}$ . The diffusion coefficients assumed those values for aqueous solution at 25 °C, according to the literature (0.025  $m^2$ /year for Ca<sup>2+</sup> and  $0.086 \text{ m}^2$ /year for Mg<sup>2+</sup>). For these four ions, both the measured and calculated results indicated that the ions are transferred from soil to the leachate liquid because the landfill soil is rich in these ions and allows leaching phenomena, as can be observed in Figs. 2 and 3.

#### 4.2. Reactive ions

The  $NH_4^+$  and  $K^+$  ions are usually referred to as reactive ones due to their typical behavior in the equilibrium batch tests. Figure 4 shows the profiles for ammonium (Fig. 4a) and potassium (Fig. 4b) with the soil and leachate

reference values shown as constants, as used in the setting initial conditions for all models. It was observed that the mass transfer model presented better agreement with experimental measurements compared with both POLLUTE and UFF- sorption predictions. For both ions, the  $D_e$  value used in the simulation was 0.010 m<sup>2</sup>/year for K<sup>+</sup> and 0.020 m<sup>2</sup>/year for NH<sub>4</sub><sup>+</sup>. In contrast to the ions presented in the last section, ammonium and potassium were transferred from the leachate to the soil with consequent contamination of the soil landfill.

Table 5 presents a comparison of values for the effective diffusion coefficients,  $D_e$ , used in the simulations and the reference values for the aqueous solution at 25 °C,  $D_0$ , according to the literature (Lerman, 1979). In this table, the D<sub>e</sub> values estimated by Pinto, 2004 (UFF sorption model), by Ritter and Gatto (2003) using Pollute and by the present model are presented. Notably, the effective coefficients far from the reference values usually indicate strong interactions of the ions and the solid leachate system and usually cause larger deviations for the isotherm sorption models or distribution coefficients formulations. In this study, only Cl did not confirm this general trend because the experimental profile presented a typical behavior for diffusionlike phenomena; therefore, for this particular behavior it is always possible to represent the concentration curves by an equivalent solution of the diffusion equation, as the literature indicates (Incropera, & Wiit, 1990).

#### **4.3.** Transient results

Figures 5, 6 and 7 show the profiles of transient ion diffusion considered in the leachate and soil landfill used in this study. The figures present the temporal evolution of the concentration profiles numerically predicted (18, 36, 54 and 72 h). The numerical values at 72 h, which are coinci-



Figure 3 - Profile of molecular diffusion for calcium (a) and magnesium (b) ions using the experimental results of 2003.



Figure 4 - Profile of molecular diffusion for ammonium ions (a) and potassium (b) using the experimental results of 2003.

**Table 5** - Comparison of effective diffusion coefficients determined in this simulation: UFF sorption model, POLLUTE, present model and  $D_0$  for ion in aqueous solution at 25 °C according the literature.

Ion	$D_e (m^2/year)^{(a)}$	$D_e$ $(m^2/year)^{(b)}$	$D_e$ (m <sup>2</sup> /year) <sup>(c)</sup>	$D_0$ $(m^2/year)^{(d)}$
Cl	0.020	0.020	0.064	0.064
$Na^{+}$	0.040	0.040	0.035	0.042
$Ca^{+2}$	0.040	0.040	0.025	0.025
$Mg^{+2}$	0.040	0.060	0.086	0.086
$K^{+}$	0.020	0.020	0.010	0.062
$\mathrm{NH}_{4}^{+}$	0.010	0.070	0.020	0.062

(a) UFF-sorption (b) POLLUTE (c) Present model and (d) the diffusion coefficient in free solution  $(D_0)$  according to the literature.

dent with the measured time, were those used to validate the model. It is interesting to note the behavior of calcium, which indicated that the ion transfer mechanism changed with time, evidenced by the changing the sign of the curves derivatives. For Na<sup>+</sup>, the experimental results showed larger variations probably due to inaccurate measurements; however, it was possible to get intermediate predictions across the measured results.

Figures 8 to 10 show the average concentration temporal evolution for interstitial leachate throughout the experimental procedure. The predicted results show the changes in ions concentrations with time and represent a measure of soil contamination with the ions and vice versa. It was observed that for Cl<sup>-</sup> the concentration profile reached a saturation point during the experiment time, while the same was not predicted for Mg<sup>2+</sup>, Ca<sup>2+</sup> or Na<sup>+</sup>.

Figure 9 shows the profiles of calcium (Fig. 9a) and sodium (Fig. 9b) ions, in which it can be noticed that stabilization was not achieved.



Figure 5 - Profile of transient molecular diffusion for chloride ions (a) and sodium (b) using 18, 36, 54 and 72 h for simulation.

In contrast to the above ions, for  $NH_4^+$  and  $K^+$ , the concentrations in the soil increased with time, indicating that these ions were transferred from leachate to soil. For both ions, the model indicated that the experimental time was not sufficient to saturate the liquids.

According to the characterization tests of the soil from the Gramacho landfill (Ritter & Gatto, 2003), the ammonium and potassium ions are in lower concentration in the soil, and the soil has large capability to absorb this ions compared to calcium, sodium, chloride and magnesium.



Figure 6 - Profile of transient molecular diffusion for calcium (a) and magnesium (b) ions using 18, 36, 54 and 72 h for simulation.



Figure 7 - Profile of transient molecular diffusion for potassium (a) and ammonium (b) ions using 18, 36, 54 and 72 h for simulation.



Figure 8 - Profile of concentration versus time for chloride (a) and magnesium (b) ions.



Figure 9 - Profile of concentration versus time for calcium (a) and sodium (b) ions.



Figure 10 - Profile of concentration versus time for ammonium ions (a) and potassium (b).

Figures 11, 12 and 13 show the rate of mass transfer of the soil interstitial liquid to the soil particles for chloride, sodium and magnesium ions. The figures show the total rate of mass transfer (a) and in the medium point inside the experimental cell (b). For both ions, the rate of mass transfer rapidly increased at the beginning of the experiment and indicated that the maximum rate could not be achieved within the experimental time and that saturation conditions were beyond of the experimental time in this study.

In contrast with Cl<sup>+</sup> and Na<sup>+</sup>, presented in Figs. 11 and 12, the Mg<sup>2+</sup> rate of mass transfer reached the maximum values and slowly decreased. However, the saturation con-



Figure 11 - Profile of the rate of mass transfer for the (a) total and (b) medium point for chloride ion.



Figure 12 - Profile of the rate of mass transfer for the (a) total and (b) medium point for sodium ion.

centration was still beyond the experimental time considered in this study, although the results indicated that the beginning of the saturation process was achieved (Figs. 13a and 13b).

Figures 14 and 15 show the rate of mass transfer of the soil particles to the interstitial liquid for the ammonium and potassium ions. The figures show the calculated total mass transfer rate (a) and the rate at the point inside the experimental cell in the vicinity of the interface soil reservoir interface (b). It can be observed that, at the beginning of the calculation, the mass transfer rate was very rapid for  $NH_4^+$  and the inversion point was rapidly achieved, initiating the saturation process. For K<sup>+</sup>, the initial stage was also rapid, and almost linear growth was observed. For both ions, the saturation concentrations were not achieved in the interval of the experimental time.

The transient calculations presented in this section can be used to predict the long-term contamination profile, although it is not shown in this study. The rate of mass transfer predicted in these calculations could be used to estimate plume contamination within the soil landfills, and therefore it is a useful tool to analyze environmental impacts on the soil. The aim of this study was to estimate model parameters and confront model formulations with experimental measurements. Features of the model such as soil saturation time and plume contamination were not explored in this study. The next step of this study is under development and consists of the application of the formulation discussed here for large-scale landfills simulations. However, due to large computation times and a need to accurately represent large domains, the MPHMTP software is being improved by implementing parallel computation techniques suitable for use in a computer cluster, which will provide spatial and time-scale calculations compatible with landfills with reasonable computation times.

## **5.** Conclusions

In this paper, a model based on mass transfer formulations was presented and discussed in light of previous models and experimental results for laboratory scale experimental procedures. The main features of MPHMTP (Multi-Phase Heat and Mass Transfer Program) were dis-



Figure 13 - Profile of the rate of mass transfer for the (a) total and (b) medium point for magnesium ion.



Figure 14 - Profile of the rate of mass transfer for the (a) total and (b) medium point for ammonium ion.



Figure 15 - Profile of the rate of mass transfer for the (a) total and (b) medium point for potassium ion.

cussed. The model was based on general transport equations of ions within the soil media and can handle several kinds of soil and barrier structures by considering the ion concentration evolution in both soil and interstitial liquids. The model predictions were compared to previous models and showed closer agreements with experimental data obtained in the Barone experimental cell using soil from the Gramacho landfill. As a baseline, the chloride, sodium, calcium, magnesium, ammonium and potassium ions were selected as representative of medium to high sorption rates in an organic soil such as that from the Gramacho landfill.

As a general trend, the model predicted results closer to the experimental measurements compared to the commercial POLLUTE software and a previously developed model based on distribution coefficients (UFF-sorption model). In the specific case of the calcium ion, strong agreement was observed regardless of the atypical behavior presented by this ion in the experimental measurements.

The results of the simulation carried out in this work confirmed that the migration process of inorganic ions from the leachate into the soil can be explained by taking into account three basic mechanisms: advection and diffusion in the liquid phase (leachate), sorption in the soil/leachate interface and diffusion in the soil particles. In contrast with previous models, this model accurately predicted the behavior of all ions presented in the diffusion experiments and showed potential for application to large time and spatial scale predictions of ion contamination in landfills.

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