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On equilibration of pore water in column leaching tests

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ABSTRACT

Column leaching tests are closer to natural conditions than batch shaking tests and in the last years have become more popular for assessing the release potential of pollutants from a variety of solids such as contaminated soils, waste, recycling and construction materials. Uncertainties still exist regarding equilibration of the percolating water with the solids, that might potentially lead to underestimation of contaminant concentrations in the effluent. The intention of this paper is to show that equilibration of pore water in a finite bath is fundamentally different from release of a certain fraction of the pollutant from a sample and that equilibrium is reached much faster at low liquid-to-solid ratios typical for column experiments (<0.25) than in batch tests with much higher liquid-to-solid ratios (e.g. 2–10). Two mass transfer mechanisms are elucidated: First-order type release (film diffusion) and intraparticle diffusion. For the latter, mass transfer slows down with time and sooner or later non-equilibrium conditions are observed at the column outlet after percolation has been started. Time scales of equilibrium leaching can be estimated based on a comparison of column length with the length of the mass transfer zone, which is equivalent to a Damköhler number approach. Mass transfer and diffusion coefficients used in this study apply to mass transfer mechanisms limited by diffusion in water, which is typical for release of organic compounds but also for dissolution of soluble minerals such as calcite, gypsum or similar. As a conclusion based on these theoretical considerations column tests (a) equilibrate much faster than batch leaching tests and (b) the equilibrium concentrations are maintained in the column effluent even for slow intraparticle diffusion limited desorption for extended periods of time (>days). Since for equilibration the specific surface area is crucial, the harmonic mean of the grain size is relevant (small grain sizes result in high concentrations even after short pre-equilibration of a column). The absolute time scales calculated with linear sorption and aqueous diffusion aim at organic compounds and are not valid for sparingly soluble mineral phases (e.g. metal oxides and silicates). However, the general findings on how different liquid-to-solid ratios and specific surface area influence equilibration time scales also apply to other mass transfer mechanisms.

1. Introduction

Laboratory column percolation tests have become more widely accepted for assessing risks of seepage and groundwater pollution by aqueous leaching of recycling materials, soils, construction products, etc. (Maszkowska et al., 2013; Krüger et al., 2013, 2012, Beyer et al., 2009). While column tests are much closer to real conditions in terms of low liquid-to-solid ratios than batch shaking tests (López Meza et al., 2010, 2008, Delay et al., 2007), they have to be operated often at higher flow velocities than present in the field because of practical reasons (duration less than a week, sufficient volume of aqueous leachate for analysis, etc., see e.g. Kalbe et al., 2007, 2008). With this, uncertainties arise about the degree of equilibration of pore water with compounds ad/absorbed to the solids. Non-equilibrium in the column effluent would lead to under estimation of the concentration that may be reached under field conditions.

Grathwohl and Susset (2009) showed how column tests can be evaluated based on the liquid-to-solid ratio and how results compare to batch leaching tests and field lysimeters. This analysis was based on well-known analytical solutions of the advection–dispersion equation, assuming that local equilibrium is fulfilled initially and during the percolation. Looking at a large data set of 92 samples (soils, demolition waste, incineration bottom ashes and industrial slag) for different solutes (e.g. chloride, sulfate, copper, and polycyclic aromatic hydro carbons) they showed reasonable good model fits assuming general equilibrium conditions in column tests initially, although non-equilibrium and thus mass transfer limited release of solutes eventually develops during leaching.

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Like depletion of a solute, mass transfer limitations will lead to a concentration decrease in the column effluent after initially higher equilibrium concentrations. In a comment to Grathwohl and Susset (2009), Guyonnet (2010) pointed out that initial high concentrations must not be missed and might be caused by initial fast release rates. In their reply, Grathwohl and Susset (2010) used numerical simulations of column leaching tests accounting for mass transfer limitations by slow intraparticle diffusion to show that initially equilibrium often exists and depending on the flow velocity after some time concentrations decrease and extended diffusion limited tailing of effluent concentrations develops. This behavior may, in principle, be fitted by the advection–dispersion equation, however, with unreasonably large longitudinal dispersion coefficients.

Overall, the goal of this paper is to show how liquid-to-solid ratios and grain size influence the time needed to achieve initial local equilibrium in the pore water in column leaching tests during pre-equilibration (which also applies for batch shaking tests: finite bath) and how long equilibrium concentrations are observed in the effluent after percolation was started. Theoretical considerations based on mass transfer principles show that bringing a given mass of solids with a certain volume of pore water to a certain degree of equilibrium, e.g. 90%, is fundamentally different from removing, e.g. 90% of a solute from solids during leaching. Two mass transfer mechanisms limiting release kinetics are elucidated: (1) film diffusion through a boundary layer of water of given thickness (first order models) and (2) intraparticle pore diffusion where diffusion distances increase with time and thus release rates decrease with the square root of time initially. Both, the pre-equilibration and dynamic leaching scenarios (after percolation was started) are discussed. Since for interface mass transfer the specific surface are is relevant, the harmonic mean of grain sizes is considered (see Appendix D).

This study applies easy-to-evaluate analytical solutions or approximations for film and intraparticle diffusion limited mass transfer, derives the crucial parameters for calculation of the characteristic times for pre-equilibration such as the liquid-to-solid ratio, and estimates realistic time scales for pre-equilibration of column tests and equilibrium conditions to be expected during percolation. The appendixes explain (A) parameter definitions in analytical solutions for equilibration in a finite bath (column pre-equilibration or batch) for film and intraparticle diffusion limited mass transfer, (B) long-term approximations for intraparticle diffusion limited desorption kinetics, and (C) Sherwood numbers to estimate film diffusion limited release in columns and. Also a table with grain size distributions of recycling materials typically used in road construction is provided (D). For poorly soluble mineral phases (quartz, metal oxides and silicates, etc.) these simple mass transfer models are not sufficient as pH and ionic strength may change with time which causes shifts in the equilibrium regime. Here numerical tools coupling chemical speciation models to transport (e.g. PHREEQC, MIN3P) can be employed (Mayer et al., 2002; Parkhurst and Appelo, 1999. However, the general conclusions concerning the influence of specific surface area and liquid-to-solid ratio on equilibrium time scales still apply. De Windt et al. (2011) e.g. use first order kinetic rate laws as derived here and apply them for mineral phases occurring in steel slag. They show that the fine grained fraction dominates equilibration of pH and inorganic species. Even when mineral phases change very slowly over time the pore water chemistry may follow that closely.

2. Pre-equilibration in column and batch tests (finite bath)

2.1. Film diffusion

Fig. 1 shows boundary conditions in a finite bath (column during pre-equilibration or batch experiment) where solute release from a grain surface is controlled by film diffusion (so-called linear driving force). The approach to equilibrium in the pore water is described by (see Appendix A for derivation of various rate parameters):

$$\frac{C_w}{C_{w,eq}} = 1 - \exp\left(-kA^o\left(1 + \frac{V_w}{K_d m_d}\right)t\right)$$
$$= 1 - \exp\left(-\frac{k6}{\rho_s d}\left(\frac{m_d}{V_w} + \frac{1}{K_d}\right)t\right) \tag{1}$$

$C_w/C_{w,eq}$ is the relative concentration in water. k is the mass transfer coefficient (e.g. in m s^{-1}) defined as the aqueous diffusion coefficient divided by a characteristic film thickness (δ; $k = D_{aq}/\delta$,). t denotes here the contact time (e.g. in seconds). A^o is the specific surface area available for diffusion per volume of water (V_w) in the column or batch system and as such is a crucial parameter also accounting for dry mass of the solids (m_d), solid density (ρ_s) and grain diameter (d):

$$A^o = \frac{m_d 6}{V_w \rho_s d} = \frac{\rho 6}{n \rho_s d} = \frac{(1-n)\rho_s 6}{n \rho_s d} = \frac{(1-n)6}{nd} \tag{2}$$

Note, the dry mass divided by the solids density (m_d/ρ_s) yields the volume of the solids in a column (which per unit volume is: $1 - n$); $6/d$ (or 3/radius) is the specific surface area of a sphere. Effective grain sizes of mixtures are represented by the harmonic mean (d in denominator), weighted according to the mass fraction of the different particle size classes. Thus small grain sizes will dominate equilibration time scales. Note, that the liquid-to-solid ratio LS ($=V_w/m_d$) in a column is given by the porosity to bulk density ratio n/ρ which for many materials in columns is approximately 0.25 ($n = 0.4$, $\rho = 1.6$) whereas in batch tests LS ratios between 2 and 10 are frequently used.
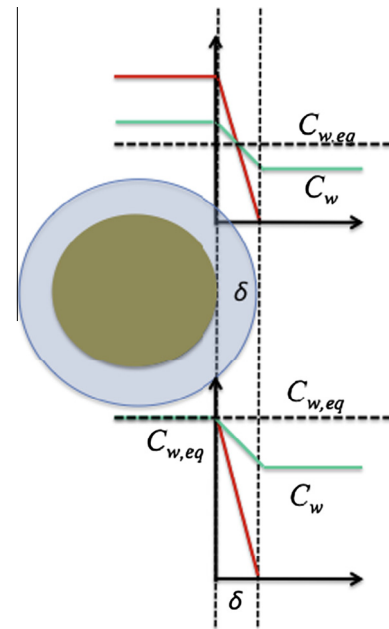

Fig. 1. Aqueous concentrations (C_w) for film diffusion (δ: film thickness) during desorption in the finite bath – horizontal dashed lines denote equilibrium ($C_{w,eq}$), red and green gradients show initial and intermediate gradients; top: significant transfer of solute into the water with decreasing concentration in solid phase; top gradients: significant transfer of solute into the water; bottom gradients: strong sorption or low amounts of water (low liquid-to-solid ratio) or stable concentrations at the solid/water interface e.g. during mineral dissolution (no or relatively little solute mass is desorbed or dissolved and goes into the aqueous phase until equilibration).