Impact of pre-equilibration and diffusion limited release kinetics on effluent concentration in column leaching tests: Insights from numerical simulations

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ABSTRACT

Column leaching tests have become a standard method for assessing leaching of pollutants from materials used, e.g., for road and railway constructions and in landscaping measures. Column tests showed to be practical in laboratories yielding robust and reproducible results. However, considerable uncertainty still exists related particularly to the degree of equilibration of the pore water with the solids during preparation (pre-equilibration) and percolation of the column. We analyse equilibration time scales and sensitivity of concentrations in column leachate with respect to initial conditions in a series of numerical experiments covering a broad spectrum of material and solute properties. Slow release of pollutants from solid materials is described by a spherical diffusion model of kinetic sorption accounting for multiple grain size fractions and sorption capacities. Results show that the cumulative concentrations are rather independent of the pre-equilibration level for a broad spectrum of parameter settings, e.g. if intraparticle porosity is high, grain size is small, or if the sorption coefficient is large. Sensitivity increases with decreasing liquid solid ratios and contact time during percolation. Significant variations with initial column conditions are to be expected for material and compound properties leading to slow release kinetics. In these cases, sensitivity to initial conditions may have to be considered.

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1. Introduction

1.1. Background

Recycling of materials becomes more and more relevant and has been put high on the political agenda. Defined goals are ambitious, e.g., the EU targets a recycling quota for construction and demolition waste of 70% by weight until 2020 (on average in EU member states) in the amended EU Waste Framework Directive (WFD) (European Commission, 2008). Largest solid waste material streams come from soil excavations, construction and demolition waste (CDW), incineration ashes (waste, coal for electrical power) and slag from various industrial sources (iron, steel, copper etc.) (European Commission, 2014). Many of these solid waste materials have properties which make them suitable for all kind of technical constructions including landscaping, roads and dams, fills for water drains, etc. (Arulrajah et al., 2012; Lupsea et al., 2014; Molenaar and van Niekerk, 2002; Rahman et al., 2014, 2015; Roessler et al., 2015). The greatest barrier for their reuse is the

potential risk of groundwater contamination, which may result from the release of pollutants into the water that percolates through the construction (Butera et al., 2014; Galvin et al., 2013; Hjelmar et al., 2007; Petkovic et al., 2004; Somasundaram et al., 2015; Susset and Grathwohl, 2011). Therefore, to guarantee a safe reuse, reliable procedures for the characterization of mineral waste materials with respect to their pollutant leaching potential are of utmost importance. Among several different leaching tests that were proposed to date, column leaching tests are supposed to come closest to natural flow conditions and are therefore believed to be most appropriate to assess the potential impacts of a re-used mineral waste in the environment (Grathwohl and van der Sloot, 2007; Grathwohl and Susset, 2009).

1.2. Existing testing standards and evaluation scheme

Standardized protocols and technical specifications were developed, which define the sample preparation rules as well as relevant parameters of the setting and operation of the leaching test, including column geometry, time period for flooding and pre-equilibration of the column, contact time during percolation, measurement intervals and mode of measured data evaluation. Table 1

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Table 1
Overview of column leaching test standards.

Method/standard	prEN 14405[a] (European Union)	FprCEN/TS 16637-3[b] (European Union)	DIN 19528[c] (Germany)	US EPA test method 1314[d] (United States of America)
Sample preparation	Use original sample if <4 mm fraction ⩾90% (small column) or if >10 mm fraction ⩽5% (wide column); Otherwise reduction of fraction >4 mm or >10 mm, respectively	Use original sample if <4 mm fraction ⩾45%; and grain size ⩽16 mm or ⩽22.4 mm (depending on column diameter); otherwise crushing of oversized material	Use original sample for d ⩽ 32 mm, reduce fraction >32 mm to add to 16/32 fraction	Fraction ⩾85% should pass 2.38 mm (U.S. No. 8) sieve; reduction or exclusion of material with d < 2.5 mm
Column dimensions	Diameter: 5 cm ("small") or 10 cm ("wide")	Diameter: ⩾5 cm	Diameter: 5 cm or 10 cm	Diameter: 5 cm
	Packing length: 30 cm ± 5 cm	Packing length: 30 cm ± 5 cm	Packing length: 20 cm to 50 cm	Packing length: 30 cm
Saturation time		4 h to 6 h	Saturate column slowly within a period of 2 h	Not specified
Equilibration time	16 h up to 72 h	12 h up to 72 h		21 h ± 3 h
Contact time, t_c, during percolation	~10 h to 24 h[e]	~5 h to 12 h[f]	~5 h	~3 to 14 h[g]
Eluate collection times	7 fractions: LS = 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0	7 fractions: LS = 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0	6 fractions: LS = 0.3, 0.5, 1.0, 2.0, 5.0, 10.0	9 fractions: LS = 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, 10.0

[a] Not implemented yet; as of 2013, also representing CEN/TS 14405.
[b] Not implemented yet; as of Nov. 2015.
[c] As of 2009.
[d] As of 2012 posted by U.S. EPA in the New Methods section of "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846).
[e] Depends on actual packing length and on porosity, n, of packed material: $t_c = 24$ h × n × L [cm]/15 cm.
[f] Depends on actual packing length and on porosity, n, of packed material: $t_c = 24$ h × n × L [cm]/30 cm.
[g] Depends on dry solid density, ρ_s, and porosity, n, of packed material, and on the effective production rate epr (0.75 ± 0.25 LS per day): $t_c = n/(epr \times \rho_s (1 - n))$.

gives an overview of the standards that are addressed in the discussion further below. Please note that the standards on the European level are still under debate and have not been implemented yet.

Typically, leaching tests are evaluated in terms of cumulative release for specific values of the liquid (L)-to-solid (S) ratio, L/S, hereafter denoted as LS (L/kg), which refers to the time after which a certain volume of liquid (i.e. water) has percolated through the column. The eluate, i.e. the solution obtained from the leaching test, is typically collected in a number of 6 to 9 separate fractions according to a predefined collection schedule (specified in terms of LS values, see Table 1). The measured concentration in these eluate fractions, c_{frac}, is then used to characterise the leaching potential of the material sample (Fig. 1).

As collection times are not equidistant, the water volume of individual fractions, $V_{w,i}$, differs and $c_{frac,i}$ values represent average concentrations for different time spans (Fig. 1a). The mass released until a certain LS value X is achieved, $M_{released,LSX}$, can be calculated by (Fig. 1b):

$$M_{\text{released},LSX} = \sum_{i=1}^{i=i(LS=X)} c_{frac,i} V_{w,i} \tag{1}$$

The corresponding cumulative concentration at LSX, $c_{cum,LSX}$, or simply the LSX concentration c_{LSX} (Fig. 1c) is:

$$c_{LSX} = \frac{M_{released,LSX}}{V_{w,LSX}} = \frac{M_{released,LSX}}{\sum_{i=1}^{i=i(LS=X)} V_{w,i}} \tag{2}$$

Finally, cumulative release might be also referred to the mass of the sample, M_s, to calculate $m_{cum} = M_{released} / M_s$ (Fig. 1d).

Expressing time in terms of LS allows transferring lab results to the field where the time corresponding to a certain LS typically is much larger than in the lab because specific discharge and seepage flow rate are by several orders of magnitude smaller. As summarized by Grathwohl and Susset (2009) several experimental studies have confirmed this transferability through comparison of lab columns (with different dimension and flow velocities) and field lysimeter results (Butera et al., 2015; Guyonnet et al., 2008; Susset and Leuchs, 2008). Particular phenomena observed under

real conditions, such as preferential flow effects (e.g., Pontedeiro et al., 2010; Trinchero et al., 2011), however, cannot be mimicked in the lab (here the goal is to get reproducible results). The time scale in the field that is associated to a certain LS value can be estimated to $T_{field} = (2.65 \times (1 - n) \times h/q) \times LS$ where n, h, and q are porosity, thickness of release zone, and infiltration rate, respectively. If infiltration rate is low and thickness of waste material is large, even low LS values may refer to several decades.

1.3. Objectives

Although column leaching tests showed to be practical in laboratories and yield robust and reproducible results, considerable uncertainty is still related to the initial conditions with respect to the degree of equilibration of pore water and solids achieved during preparation (pre-equilibration) and during percolation with increasing LS ratios.

In this study, in an attempt to extend and generalize the findings from Grathwohl (2014), and to systematically investigate the sensitivity of leaching tests results to given initial conditions, we performed a series of numerical experiments on diffusion-limited release of compounds from a variety of uniform and non-uniform materials. The aim was to elucidate equilibration time scales in laboratory column tests representing typical test set-ups according to the German standard DIN 19528 (2009), and to analyse leaching behaviour as a function of pre-equilibration level and material properties. Since most of the recycling materials show slow release from internal pore spaces we focus our study on intra-granular diffusion, which is often limiting pollutant release during percolation of such materials. To account for other relevant standards that set technical specifications for column leaching tests being different from the German standard (Table 1), we selectively also deviate from German standard test-setup parameters and procedures.

Initial conditions in the column may by quite complicated and specific to the particular test settings, namely to the time of column flooding and subsequent equilibration time (e.g., if sorption is low and equilibration fast then the inlet part of the column may already be depleted and compound mass be accumulated at