Stationary and self-forming liners around waste deposits: Formulation of release reduction and characterization by radiotracer experiments

H. A. Das
Department of Geochemistry, Faculty of Earth Sciences, Utrecht University, P.O.Box 80.021, 3508 TA Utrecht, The Netherlands and Netherlands Energy Research Foundation ECN, P.O.Box 1, 1755 ZG Petten, The Netherlands

(Received July 1, 1998)

Reduction of the diffusional emission of trace constituents from wetted granular waste by application of different types of liners is formulated, which enables their mutual comparison. Laboratory procedures for the measurements of the involved parameters are discussed, together with some examples.

Introduction

Emission-rates from waste dumps by leaching and diffusion can be reduced by surrounding barrier layers, often called liners. They are of three kinds: (1) artificial barriers, consisting of concrete, cement, organic resins or plastics with a thickness varying from a few millimetres up to ~2 cm,\(^1\) (2) layers of naturally occurring materials like clay, hydrated iron oxide, bentonite or jarosite,\(^2,3\) and (3) self-forming and -healing thin liners, consisting of a sparingly soluble compound like calcium carbonate or gypsum, caused by the presence in or the admixture to waste material and surrounding material.\(^2-4\) Field applications of these three options are reported in literature, e.g., in References 1-3, 5 and 6.

This text focuses on two aspects of liners: (1) the formulation of the reduction in the emission-rate in terms of a (usually time-dependent) "advantage factor" defined as the ratio of the integrated outward flux per unit surface area without and with the liner, based on the mathematical formulation of diffusion as summarised in References 8, and (2) the use of benchtop (radiotracer-) experiments for the assessment of emission-rate and advantage factor. This combined approach enables a preliminary choice and its subsequent testing in the laboratory.

Advantage factor

Assumptions

The present approach is subject to some basic assumptions: (1) a homogeneous, wet, mass of granular waste is contained by a barrier layer which is in turn surrounded by a homogeneous, wet, medium. There is no net flow of water; (2) concentrations of microconstituents in the interstitial water of the waste body remain constant, (3) emission occurs by diffusion through the barrier into the environment, (4) the effective diffusion coefficients of a microconstituent in barrier layer, \(D_1\), and that in the adjacent environment, \(D_2\), are governed by the effective porosity, the tortuosity of the material and the eventual reversible adsorption, (5) the effective porosity refers to the through-going pores only, (6) in case of self-forming liners, thickness increases with time.

The determination of the effective diffusion coefficient by laboratory radiotracer experiments in a miniature contraption has been reported elsewhere.\(^9\) The influence of the water contents is formulated in Reference 10.

Artificial barriers of constant thickness

The computation of the advantage factor, \(R\), is summarized in Appendix 1. The governing dimensionless parameters are

\[
x = \left( \frac{D_1 \cdot t}{\ell^2} \right)^{0.5}
\]

\[
y = \left( \frac{D_2 \cdot t}{\ell^2} \right)^{0.5}
\]

where \(D_1\) and \(D_2\) are the effective diffusion coefficients in barrier layer and surrounding material, in \(\text{cm}^2 \text{s}^{-1}\), \(t\) is the contact time in seconds and \(\ell\) the layer thickness in cm.

The values of \(D_1\) and \(D_2\) are determined by the respective effective porosities, \(\varepsilon'\) and tortuosities, \(\xi\) of barrier layer and surrounding material, that is by the retardation factor \(\varepsilon'/\xi\). Thus it is often possible to make a priori estimates of the orders of magnitude of \(D_1\) and \(D_2\).

Figure 1 gives \(R\) as a function of \(\ell\) and \(t\) for \(D_2 = 5 \times 10^{-6} \text{cm}^2 \text{s}^{-1}\) and \(D_1/D_2 = 10^{-2}; 10^{-3}\) and \(10^{-4}\). The (constant) value of \(\ell\) is 0.25, 0.50 and 1.0 cm while times of up to 20 years are considered. The choice of \(D_2\) follows from earlier determinations on granular material.\(^9\)
The initial maximal value of $R$ is $(D_1/D_2)^{1/2}$. Its gradual decrease is a common feature of all barrier layers of constant thickness. It becomes less marked with increasing thickness.

**Self-forming and -healing liners**

Diffusion with simultaneous bimolecular chemical reaction is treated in textbooks on transport phenomena, e.g., in References 11 and 12. The governing parameter is the reaction rate constant. The formulation given in Appendix 2 applies to the case of instantaneous reaction. It is assumed that both reactants continue to diffuse into the already existing layer of precipitate. The assumption of immediate reaction implies linear diffusion profiles (cf. Fig. 2a). If only one reactant diffuses into a medium with an excess concentration of the other reactant this may affect the value of the diffusion coefficients and thus that of $K$ in Eq. (2.6).

The principal difference with a liner of constant thickness is a constant value of the dimensionless parameters $x$ and $y$. This implies a constant advantage factor.

A case in point is the formation of a layer of CaCO$_3$ from counter-diffusion of CaCl$_2$ and Mg(NO$_3$)$_2$. The values of the diffusion coefficients in dilute aqueous solution are $1.15 \times 10^{-5}$ and $0.72 \times 10^{-5}$ cm$^2$ s$^{-1}$, respectively. The density of CaCO$_3$ is taken as $\rho = 2.71$ g cm$^{-3}$. Again it has been assumed that $D_2 = 5 \times 10^{-6}$ cm$^2$ s$^{-1}$. For any arbitrarily taken value of $D_1/D_2$ one may now compute the time dependency of $\ell_t$ and the advantage factor, if the (constant) concentrations of the reactants in the two adjacent media are known. Figure 3 gives the advantage factor for the ranges $10^{-4} < D_1/D_2 < 0.4$ and $2 \times 10^{-3}$ g cm$^{-3} < (C_A)_0 = (C_B)_0 < 1$ g cm$^{-3}$. The growth of the layer thickness varies from $\ell_t = 10^{-6}$ cm at $D_1/D_2 = 10^{-4}$ and $(C_A)_0 = (C_B)_0 = 2 \times 10^{-3}$ g cm$^{-3}$ to $\ell_t = 1.5 \times 10^{-3}$ cm for $D_1/D_2 = 0.4$ and $(C_A)_0 = (C_B)_0 = 1$ g cm$^{-3}$; $t$ is expressed in seconds.

The calculated data serve as a first approximation only. The growth of the liner should be measured experimentally, as the formulation of Appendix 2. assumes a 'smooth' layer without any irregularities. This implies the substitution of the derived equation $\ell_t = (2K)^{1/2} t^{1/2}$ by the semi-empirical relation $\ell_t = \beta t^{1/2}$.

**Barriers of naturally occurring, adsorbing, materials**

A thick adsorbing layer imposes steady state diffusion. This also holds for its combination with a thin liner. Here, two quantities are of practical interest: (1) the time $T$ at which emission from the adsorbing layer into the environment starts, and (2) the time-dependence of the emission-rate from $T$ onwards. Figure 2b schematizes the situation, while Appendix 3 gives the pertaining formulation. The advantage factor may reach high values.