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Lysimeter studies to investigate the leaching of ^{241}Am from low level radioactive waste

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Abstract

Radionuclide release terms are important input data for the mathematical modelling of radioactive waste disposal systems. BNFL have conducted replicate lysimeter experiments to simulate unsaturated trench conditions using waste materials artificially contaminated with ^{241}Am in order to overcome the difficulties encountered in obtaining quantitative release data for actinides using real LLW samples. The observed results show that the waste leachate is acidic and reducing. Americium release conforms to a typical bimodal pattern. The radionuclide release data have been simulated using a dual porosity contaminant transport model (DUOPOR) developed by BNFL. The modelling studies help identify the processes controlling the different phases of radionuclide release. Geochemical modelling reveals that leachate Am concentrations are orders of magnitude below the predicted solubility limit indicating that solubility is not controlling release. © 1998 Elsevier Science S.A.

Keywords: Americium; Lysimeter; Low Level Radioactive Waste; Dual porosity

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1. Introduction

Lysimeters are widely used to investigate the release of contaminants from waste or soil samples and also for waste degradation studies [1–3]. BNFL have carried out a substantial lysimeter research programme simulating low level radioactive waste (LLW) trench disposal systems to derive radionuclide release terms [4,5]. These experiments have traditionally used real waste samples as substrates for leaching studies but the very low actinide concentrations in typical LLW have not led to accurate release terms for these elements. To overcome this difficulty, BNFL have conducted a recent study with non-active waste materials artificially spiked with ^{241}Am. Three identical lysimeters have been operated to check the variability of the results. As well as generating source terms for assessment modelling, these experiments are designed to develop a more mechanistic understanding of the physical and chemical processes which control radionuclide release from unsaturated waste systems in order to assist conceptual model development.

2. Experimental

The three replicate lysimeters, labelled Am1, Am2 and Am3, were small-scale, gas-tight columns made from PVC tubing. A schematic representation is given in Fig. 1. The diameter of each lysimeter was 20 cm; the waste was packed to a height of 38 cm giving a waste volume of 12 l and head space volume of 1.4 l and each contained 1.44 kg of waste at a density of 120 kg m^{-3}. The lysimeters were filled with waste materials typical of LLW from the Sellafield site, such as rubber gloves, plastic bottles and bags, PVC sheeting, metal washers, paper, card and tissues. The composition of waste placed in each lysimeter was as follows: 40% cellulosics; 40% plastics; 10% rubber; 10% metal. Waste spiking was carried out during waste loading. The non-active materials were shredded, mixed and added in small batches to the lysimeter. As each batch was added, a radionuclide spike solution was sprinkled onto the waste to spread the radionuclide inventory as evenly as possible. The initial inventory of ^{241}Am in each lysimeter was 7.5×10^5 Bq, equivalent to a concentration of 6.3×10^7 Bq m^{-3}. After loading, the lysimeters were sealed gas tight and fitted with a fermentation lock to prevent a build-up of internal gas pressure and then operated in conventional single-pass mode. The leachant

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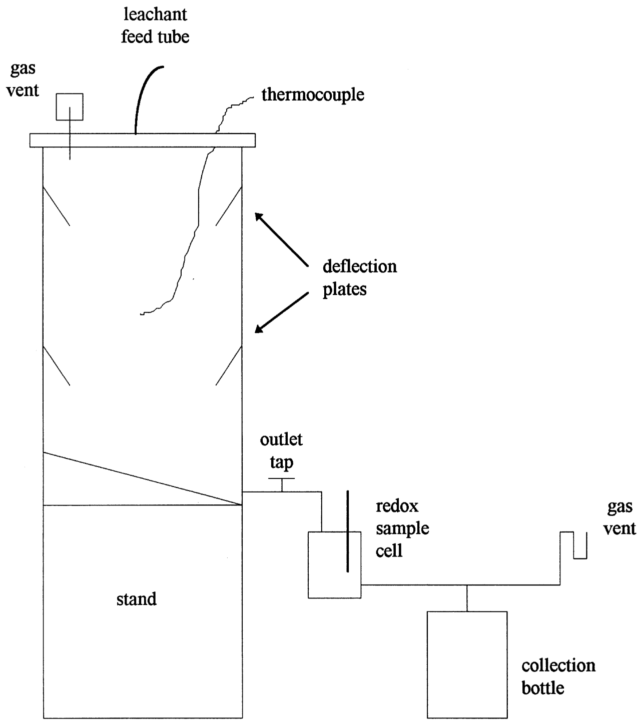

Fig. 1. A schematic diagram of a lysimeter.

was rainwater, eluted through plastic drums containing rock fragments, soil and gravel to simulate water passing through an engineered cap. The irrigation rate was based on a rainfall rate of 1 $\mathrm{m\,a^{-1}}$ with no allowance for evaporation. The lysimeters were designed to simulate unsaturated conditions. The required volume of leachant was added daily in a fixed time period (~4 h) using a peristaltic pump and the leachate produced was allowed to constantly drip out of the columns to prevent ponding and the formation of saturated conditions. Internal deflection plates were included to direct water flow back into the waste and minimise wall effects. A sloping base directed flow towards the outlet tap. Leachate redox was monitored in a sample cell attached to the lysimeter outlet tap prior to exposure to the atmosphere (see Fig. 1). The lysimeters were operated for 60 weeks.

3. Data analysis-the dual porosity model

Investigation of the impact of structured media on solute transport [6] has shown that the presence of low permeability domains such as stratified layers can cause non-ideal transport of solutes as exemplified by asymmetrical breakthrough curves (BTCs). A major characteristic of many structured media is the existence of preferential pathways where advection dominates transport with diffusive mass transfer between domains which are advection dominated (the mobile zone) and those that are not (the immobile zone). For the lysimeters considered here 1D, steady-state, water flow is assumed with advective-dispersive flux confined to the mobile zone. The equations for a dual-porosity mobile-immobile solute transport model are [6]:

$$\beta R\frac{\partial C_{\mathrm{m}}}{\partial T}+(1-\beta)R\frac{\partial C_{\mathrm{im}}}{\partial T}=\frac{1}{P}\frac{\partial^2 C_{\mathrm{m}}}{\partial X^2}-\frac{\partial C_{\mathrm{m}}}{\partial X} \tag{1}$$

$$(1-\beta)R\frac{\partial C_{\mathrm{im}}}{\partial T}=\omega(C_{\mathrm{m}}-C_{\mathrm{im}}) \tag{2}$$

which contain four experimental variables besides C_{m} and C_{im} (solute concentrations in the mobile and immobile domains respectively), X (depth down the lysimeter) and T (time). Of the experimental parameters P is the column Peclet number, R is the retardation factor. If we have equal retardation factors for the two domains, then β and 1-β denote the relative fractions of mobile and immobile water respectively whilst ω is the Damkohler number and represents mass transfer of solutes between advective and non-advective domains. Eq. (1) and Eq. (2) apply to the case of solution transport through a lysimeter and the CXTFIT program [7] is a prominent method for determining transport parameters from observed BTCs of an elution pulse. Initial conditions for Eq. (1) and Eq. (2) have been modified here to allow solute to be disposed between mobile and immobile domains of a porous medium and hence represent initial lysimeter conditions at onset of elution with uncontaminated leachant. This modification has been made by introducing two new parameters: $\eta = C_{\mathrm{m}}/C_{\mathrm{im}}$ to describe the initial ratio of solute concentration in mobile and immobile domains and C_{total} the effective initial uniform contaminant concentration. Solutions to Eq. (1) and Eq. (2) by finite-difference methods are well established and inclusion of the new parameters, η and C_{total} to describe the initial conditions has been embodied in the DUOPOR numerical model developed by BNFL. DUOPOR predictions for the case of elution of a solution pulse show excellent agreement with analogous results using CXTFIT.

4. Results

Lysimeter leachate pH and redox profiles are shown in Figs. 2 and 3 and reveal a gradual fall in pH to a minimum around 5. The redox shows a rapid fall and reducing conditions are maintained for most of the experiment. These results have been attributed to the biological and chemical degradation of the waste, particularly the cellulose component, in a series of linked processes: hydrolysis; denitrification; sulphate reduction; acidogenesis; acetogenesis. Oxygen and other terminal electron acceptors are consumed and the main end products are carbon dioxide and acetic acid which both contribute to lowering pH. Headspace gas composition measurements for all the lysimeters yielded low oxygen levels ($<1\%$) and CO_2 values greater than 20% throughout the experiment. Table

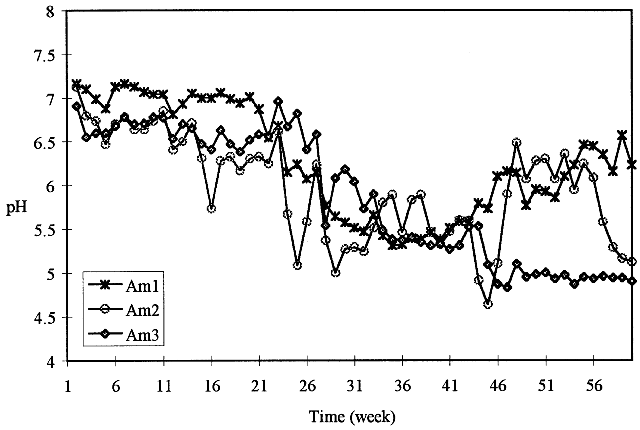

Fig. 2. Lysimeter leachate pH as a function of time.

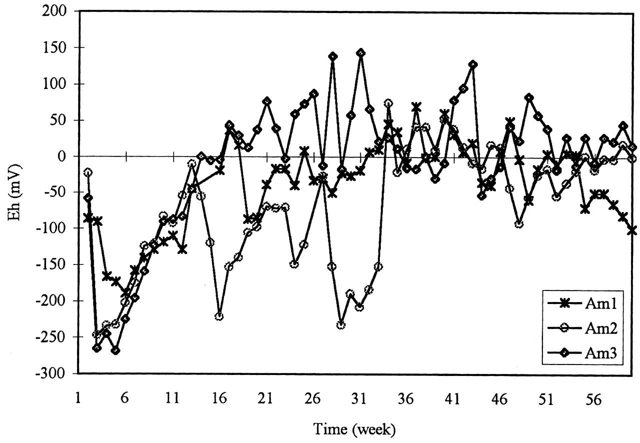

Fig. 3. Lysimeter leachate redox as a function of time.

1 shows that, relative to the input leachant, the lysimeter leachate has low levels of nitrate and sulphate and high concentrations of acetic acid. Iron levels are also higher indicating that metal corrosion may also contribute to the prevalent reducing conditions. Table 1 also shows that the americium-spiked waste produced similar leachate to real LLW lysimeters. Some of the lysimeters exhibited rising pH towards the end of the study which is often indicative of methanogenesis onset but only low levels of CH_4 (up to 2%) were recorded. These observations are similar to other larger scale lysimeter studies [1,3]. No significant difference was observed between external and internal lysimeter temperatures indicating that the waste degradation processes do not affect the ambient temperature. This has important consequences for key process rates, e.g. corrosion and cellulose hydrolysis. Fig. 4 shows cumulative ^{241}Am release over time for each lysimeter expressed as a fraction of the starting inventory. The typical release pattern is bimodal, with relatively large initial leaching followed by more constant long term release. Initial release

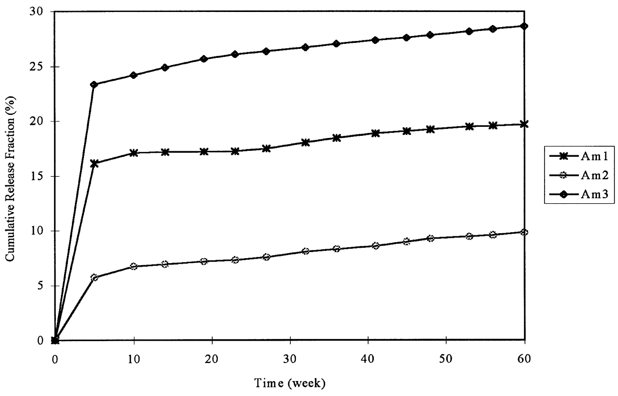

Fig. 4. Lysimeter leachate Am-241 cumulative release fractions with time.

Table 1
Mean input leachant and output leachate chemical data and ranges

Parameter	Input leachant	Americium Lysimeters leachate	Real waste Lysimeters leachate
pH	7.54±0.98	6.03±1.36	6.4±0.33
Eh (mV)	371±219	−39±170	123±152
p*E*	6.27±3.7	−0.67±2.87	2.08±2.57
Conductivity (mS cm^{-1})	0.63±1.22	1.73±2.96	0.6±1.1
Na (mmoles l^{-1})	0.80±0.53	0.40±0.03	1.07±0.56
K (mmoles l^{-1})	0.16±0.36	0.11±0.10	0.24±0.35
Ca (mmoles l^{-1})	2.61±2.85	5.17±1.50	2.69±4.71
Mg (mmoles l^{-1})	0.56±0.53	0.45±0.13	0.52±0.43
Fe (mmoles l^{-1})	0.061	0.49±0.44	0.07±0.16
Cl (mmoles l^{-1})	1.19±1.46	0.54±0.23	1.17±0.89
SO_4 (mmoles l^{-1})	2.27±3.44	0.12±0.37	0.14±0.16
NO_3 (mmoles l^{-1})	0.16±0.32	0.056±0.14	0
TIC (mmoles l^{-1})	2.47±2.04	9.34±2.40	4.27±5.28
Acetic acid (mmoles l^{-1})	0	16.0±7.6	no data
Propanoic acid (mmoles l^{-1})	0	0.20±0.06	no data
Butyric acid (mmoles l^{-1})	0	0.16±0.19	no data
Valeric acid (mmoles l^{-1})	0	0	no data

is attributed to the washout of the easily accessible sources of contamination. This is largely controlled by physical processes and is dependent on preferential pathways and the arbitrary distribution of the ^{241}Am through the heterogeneous waste. Not unexpectedly the lysimeters show notable variations although there is a strong degree of consistency in trend and absolute value.

Model effectiveness is best demonstrated by use of independently obtained parameters and comparison of predictions with experimental data. A previous pilot study, using a non-reactive tracer material (KCl), generated BTCs from which estimates for some of the parameters, i.e. P and ω, were possible using the CXTFIT program. The influence of the three remaining parameters β, R and η was the subject of a sensitivity study of their effect on the release fraction curve for which Fig. 4 is an experimental example. As previously noted the release fraction curve has a bimodal form with four key features which were found to have the following dependencies:

- a cumulative short term release (β and η dependence)
- a cumulative long term release (R and ω dependence)
- a short term release rate (R dependence)
- a long term release rate (ω dependence).

Best fit results with the DUOPOR model (using trial and error for β, R and η) indicate the need for $\eta \cong 10$ to simulate the results shown in Fig. 4. This value of η together with data for the volumes of the mobile and immobile domains implies that up to 26% of the ^{241}Am emplaced in the lysimeter resides initially in the mobile domain. This enhanced presence of ^{241}Am in the mobile regime is in turn responsible for the initial washout of contaminant.

Long term release will be controlled by physical and chemical processes, particularly sorption and the transfer of contaminant from immobile to mobile water. Fig. 5 presents ^{241}Am release fractions for the period after initial washout and shows good agreement between the replicate lysimeters. Geochemical modelling using the PHREEQE code [8] has been used to predict solubility limits based on the solution chemistries presented in Table 1 assuming $AmOHCO_3$ to be the solubility limiting phase. Modelling predicts concentrations around 10^{-7} to 10^{-8} mol l^{-1} at near neutral pH with Am carbonate species dominant in solution. The solubility rises to 4×10^{-4} mol l^{-1} for the acidic, reducing conditions observed for most of the experiment with the uncomplexed Am^{3+} ion the principle species in solution. The observed results showed a maximum ^{241}Am concentration of 3×10^{-9} mol l^{-1} for Am3 in the initial phase, with all the lysimeters yielding concentrations around 3×10^{-11} mol l^{-1} for most of the experiment, i.e. well below the solubility limit predicted. This is a consequence of a heterogeneous unsaturated waste system and the dominance of physical processes. The results suggest that performance assessment models which calculate release based on contaminant solubility limits will be conservative and are unlikely to underestimate the risk.

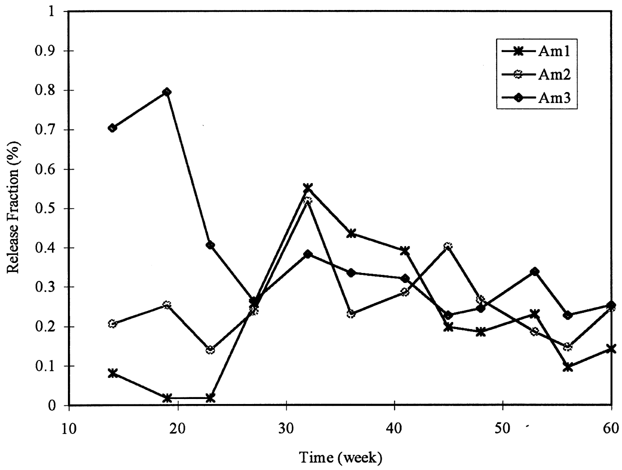

Fig. 5. Lysimeter leachate Am-241 release fractions after initial release.

5. Conclusion

An experimental protocol has been developed for small scale actinide bearing lysimeters which gives reproducible behaviour and good agreement with larger scale tests. A dual porosity mathematical model has been developed which captures the key features of the bimodal release curve by use of a mixture of prior data and sensitivity study. Work is ongoing to provide release terms for other actinides and to supply measured values for all the model parameters.

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