Application of radioanalysis to the transport of micro-constituents by diffusion

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Abstract Predictions on the leaching behaviour of microconstituents from dumped, stored, or immobilised wastes are based on estimates of the effective diffusion coefficients involved, which usually range from $\sim 10^{-6}$ to $\sim 10^{-12}\,cm^2 \cdot s^{-1}$. Radioanalysis, especially radiotracer procedures, can be applied to determine these parameters on small (field) samples of granular material and test specimens of immobilised wastes. A summary of standard experiments for both types of material under non-steady state and steady state conditions is presented

Keywords Radioanalysis, Radiotracer, Micro-constituents, Diffusion coefficient

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1 SURVEY

The assessment of environmental risks from waste disposal, storage or reprocessing depends on knowledge of the effective diffusion coefficients of the (micro-)constituents involved. Their measurement on small aliquots of granular waste and soil, or on test specimens of solidified waste as well as on artificial or naturally formed liners, is a current challenge to the radioanalyst.

This text gives a survey of the radiotracer practice developed in our laboratories over the preceding two decades in measurements on five types of material:

(1) Granular inorganic wastes.

(2) Wastes immobilised in blocks of cement or concrete.

(3) Thin layers of some plastic material used as artificial liners in waste storage.

(4) Self-forming liners at the contact surface of granular waste and surrounding soil during their formation.

(5) Cores taken from a naturally formed liner.

The underlying mathematical formulations are available upon request. A survey of the mathematics of diffusion is given in Ref.[1].

The restriction of radiotracer procedures to microconstituents in interstitial fluids avoids the difference which otherwise could be expected between the coefficients of mutual and self-diffusion[2,3].

Experimental determinations of effective diffusion coefficients refer to non-steady state as well as steady state situations, depending on whether the concentration profile

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is curved or straight. The latter case is met in diffusion through a flat layer under equilibrium conditions with constant concentrations at both sides, as in thin plastic layers and self-forming liners. Knowledge of the current type of diffusional transport is essential in the evaluation of the experimental data. Routine procedures have been developed for the following cases:

Non-steady state diffusion

(1) Granular waste in a cylindrical tube with one flat side exposed.

(2) Cubes of immobilised wastes, exposed on one side or totally immersed in leachant.

(3) A circular slice of immobilised waste with covered rim.

Steady state diffusion

(1) Granular waste in a cylindrical tube with one flat side exposed.

(2) Cubes of immobilised waste, exposed on one side to the leachant.

(3) Spheres of immobilised waste, immersed in the leachant.

Measurement of the effective diffusion coefficient, D', [$cm^2 \cdot s^{-1}$], refers to three deviations from the tabulated diffusion coefficient in dilute aqueous solution, D_o, [$cm^2 \cdot s^{-1}$]: (a) The effective porosity, ε, [-], (b) The physical restriction factor or tortuosity, ξ [-], (c) The influence of eventual interaction with the solid, expressed by a factor $(1+K)^{-1}$, where the dimensionless parameter K is the product of an in situ distribution coefficient and the local solid/liquid ratio.

Numerical values of D' range from about $10^{-6}\ cm^2 \cdot s^{-1}$ for granular materials to about $10^{-8}\ cm^2 \cdot s^{-1}$ for immobilised wastes, about $10^{-10}\ cm^2 \cdot s^{-1}$ for self-growing barriers, and about $10^{-12}\ cm^2 \cdot s^{-1}$ for plastic liners. In case of granular or immobilised wastes, D' varies considerably with the pore water content[4]. This means that the water content of test specimens has to be adjusted prior to the experiments. For granular materials this implies long time exposure to an atmosphere of known humidity, followed by mixing and determination of the water content. Measurements on immobilised wastes require previous saturation of the through-going pores. Details are available upon request.

2 APPLICATION OF RADIOANALYSIS

2.1 General

Emission or absorption of microcomponents is a slow process, proportional to the square root of contact time, and so is any related experiment. This presses for sensitive measurements of the eluted or adsorbed mass.

Both radiotracers and activation analysis can be applied in measuring mass transfer. Tracers are used in laboratory experiments, while neutron activation analysis, eventually after preconcentration, serves in field experiments.

Diffusion coefficients have been measured by radiotracer procedures in a wide variety of well-defined matrices[5,6].

The criteria for a radiotracer experiment are sensitivity in counts per microgram

and total activity within the existing laboratory license. The latter sets a limit of about 10^{10} Bq (desintegration per second) for a specialised radiotracer laboratory. If the concentration of the microconstituent involved is 10 $\mu g \cdot g^{-1}$ and 1% of its mass is transferred over a phase border to be divided into 10 fractions, which are counted each for 10^4 seconds with an overall efficiency, including gamma-ray abundance, of 5×10^{-4} c.(des^{-1}) the requirement of $\geq 10^3$ counts per fraction is equivalent to a total activity of about 2×10^9 Bq.

The required specific activity of the microconstituent is inversely proportional to the mass of the aliquot and the concentration of the microconstituent. With 10 $\mu g \cdot g^{-1}$ in an aliquot of 10 g this gives its specific activity $(Q_{sp})_{microconstituent} \geq 2 \times 10^{13}$ Bq$\cdot g^{-1}$, a value which is well within the commercially available range.

2.2 Non-steady state diffusion in granular material[7]

The practical use of the procedure is governed by the availability of suitable radiotracers and the fact that, preferably, a molecular tracer should be used to exclude electrostatic interactions. The use of ^{3}H ($T_{1/2}$=12.3 y) as HTO (tritium labelled water), $^{22}Na^+$ ($T_{1/2}$=2.6 y) as cation and NO_3' (to be determined spectrophotometrically) as anion may serve to probe charge effects.

Available tracers for probing possible distribution ratios are $^{74}AsO_3''$, $T_{1/2}$=17.7 d; $^{75}SeO_3''$ and $^{75}SeO_4''$, $T_{1/2}$=120 d; $^{99}MoO_4''$, $T_{1/2}$=67 h; $^{115m}Cd^{II}$, $T_{1/2}$=44 d and $^{124}SbO_3'''$, $T_{1/2}$=60.3 d. It follows from our experiments that there is virtually no isotopic exchange between the two selenium ions.

In practice, 3 g of (wetted) material are spiked. If an addition of $\leq$1% of the available mass is accepted, and if down to 1% of the added activity is to be detected within a counting period of 30 min at a geometry of 50%, one gets $Q_{sp} \geq 3 \times 10^2/c'$ (Bq$\cdot g^{-1}$), where c' is the ppm-concentration of the available fraction of the element. For sodium c' is of the order of 100$\mu g \cdot g^{-1}$, while for the trace constituents it may vary from ~20$\mu g \cdot g^{-1}$ downwards. Thus the specific activity of ^{22}Na should be $\geq 3.10^6$ Bq$\cdot g^{-1}$, while that of the other radionuclides should be $\geq 3 \times 10^8$ Bq$\cdot g^{-1}$.

About 3 g of the material under investigation is mixed with 0.9 mL of a carrier-free radiotracer solution, of which the chemical form is known and the specific activity allows detection in sliced segments at 10^{-2}% of the originally added activity level. The mixing of tracer and solid with a spatula is continued for at least 5 min to obtain a homogeneous paste. The consistency of the paste should be such that no liquid is spilled upon introduction in the diffusion tube. In practice this always implies unsaturated conditions.

The diffusion tube consisting of polyethylene tubing (ϕ=8 mm, l=70 mm) is marked on the non-active side (Fig.1). On that side a piston is inserted and the tube is filled with untreated, wetted material up to a length of 25 mm with a consistency similar to that of the labeled material (water content: 25% W/W). The interface is kept as smooth as possible. Since the interface is not visible, an interface marker is introduced. For this

purpose a ^{170}Tm ($T_{1/2}$=128 d, E_γ=84 keV) spike of high specific activity is used.

To avoid addition of water, the interface is marked by wetting a small rod with a ^{170}Tm spiking solution, removing the attached water droplet and lightly touching the smooth interface of the untreated segment. Subsequently, the labeled material is added up to a total length of 50 mm and the second piston is put in position.

The tubes are stored in an atmosphere of the appropriate water content. Redox sensitive materials, like bottom sediments and sludges, have to be kept in an N_2 atmosphere. Oxidised materials, liable to reduction, are treated with $\leq$10 mg $NaNO_3 \cdot g^{-1}$ to inhibit biological activity.

After a suitable storage time, usually from 10 days to 4 weeks, the combined segments are pressed out on the non-labelled side and sliced into sections of 0.5~1 mm. These are transferred to pre-weighted 8×50 mm counting tubes, dried at 85°C and weighted. The mass of the slices and the total mass of the tube contents are used to calculate the axial length of each slice. Counting is performed with an intrinsic Ge-detector connected to a MCA. Data are read into a microcomputer and processed by a programme that applies fitting of the counting result versus the square of the distance according to the pertaining profile equation given in Ref.[8]. The uncertainty is ~0.1 in the pD′-value.

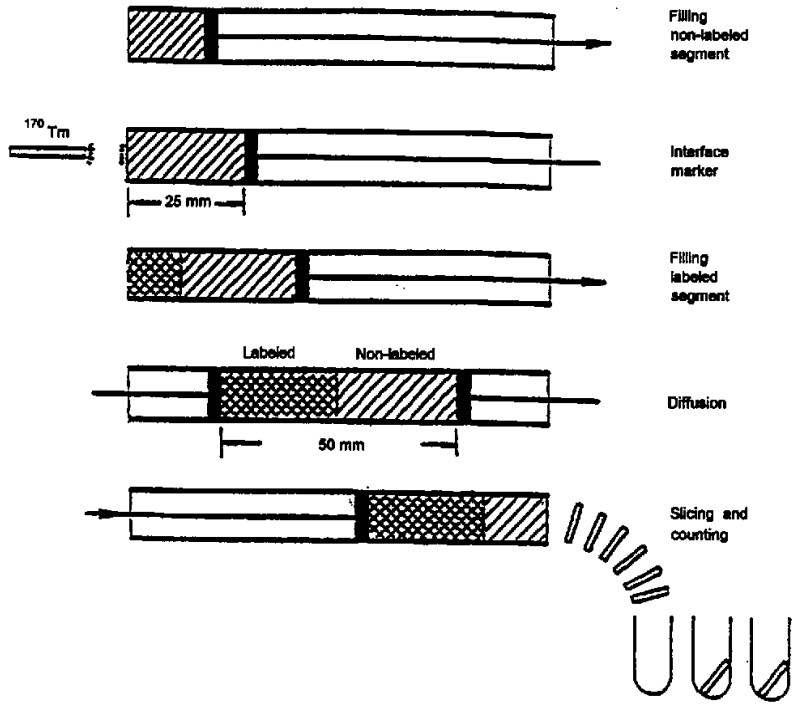

Fig.1 Experimental procedure of the diffusion tube measurements on granular solids

From the D'-values for the non-reactive radiotracers Na^+, NO_3' and SeO_4'', it is possible to estimate the tortuosity which is of the order of 2.5~3 for most granular materials.

2.3 Steady state diffusion in granular material. The growth of a self-forming liner[9]

Two reactants, which meet at the interface of dumped granular waste and surrounding soil, may give rise to a layer of precipitate. Its thickness is proportional to the square root of contact time. Radiotracer experiments in small diffusion tubes, like described in the previous section, may serve to determine the layer thickness as a function of time and thus the experimental value of the constant of proportionality. This procedure provides a check in theoretical predictions.

A case in point is the formation of a layer of $CaCO_3$ from counter-diffusion of $CaCl_2$ and $Mg(CO_3)_2$. For a self-forming and -healing liner of $CaCO_3$, formed by the diffusion of about $0.5\,g{\cdot}cm^{-3}$ $Ca(OH)_2$ into Mg^{++}-rich harbour sediment, the liner-thickness in cm was found to increase as $10^{-4} \cdot t^{1/2}$ with the contact time t in seconds.

2.4 Non-steady state diffusion from immobilised waste[10]

Only some main conclusions are given here:

(1) Leaching behaviour of immobilised waste can be examined best on cubic specimens of 5 cm side or discs of 5 cm radius and 2 cm thickness with covered rim in $\geq$200 mL leachant.

(2) The effective diffusion coefficient of a micro-constituent can be derived from its concentration in the leachant as a function of time and the initially available concentration in the solid.

The latter quality can be obtained from a cascade experiment in which a radioactivated aliquot of the granulated solid is leached with successive equal volumes of leachant.

(3) Precision increases with contact time and decreases with the effective diffusion coefficient itself. At the minimal leachant volume of 200 mL, the relative standard deviation in D' goes from ~10% at $D'=10^{-6}\,cm^2{\cdot}s^{-1}$ to ~20% at $10^{-8}\,cm^2{\cdot}s^{-1}$ for the standard cube, and from ~7% to ~15% for the standard disc.

(4) The relative precision and bias in the determination of the initially available concentration are ~ 5%.

(5) Tortuosity measurements by way of a non-reactive radiotracer feature a relative precision of 10%–20%.

2.5 Steady state diffusion from immobilised waste

The concentration of a sparingly soluble (micro-)constituent in the pore water is constant while that in the leachate remains virtually zero. In this case steady state diffusion prevails and the release from a semi-infinite specimen, like a cube or a cylinder

with one flat side exposed, is proportional to the square root of leaching time. The effective diffusion coefficient can be derived from the experimentally determined constant of proportionality.

As a case in point, the leaching of traces of heavy metals from sulphide containing cement can be mentioned[11]. Using radiotracers, effective diffusion coefficients down to $\simeq 10^{-12}\,cm^2 \cdot s^{-1}$ were determined.

3 CONCLUSION

Radiotracers and, to a lesser extent, radioactivated aliquots can be applied in determining the effective diffusion coefficients of microconstituents in (field) samples of granular materials and test specimens of immobilised wastes.

The present text gives the outlines of available detailed procedures.

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