Radionuclide transport in a single fissure. A laboratory study

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SUMMARY

Radionuclide migration have been studied in natural fissures oriented parallell to the axis of granite drill cores. A short pulse of the radionuclides solution was injected at one end of the fissure and the temporal change in radionuclide concentration of the eluate measured. After several hundred fissure volumes water had been pumped through the fissure following the radionuclide pulse the activity distribution on the fissure surfaces was measured. From the retardation of ^{152}Eu, ^{235}Np and ^{237}Pu it is concluded that these radionuclides are transported in the oxidation states Eu(III), Pu(IV) and Np(V).

The distribution coefficients K_d calculated from flow and activity distribution data on the basis of geometric surface area/volume ratios are of the same order as published K_d values obtained from batch equilibrium experiments.

INTRODUCTION

The transport of radionuclides with groundwater in geologic media is largely determined by processes such as sorption, ion exchange, precipitation, complexation and hydrolysis.

For radionuclides such as actinides with more than one possible stable oxidation state the chemical conditions, e g redox potential, pH and concentration of complexing anions are of great importance. For the understanding and possible prediction of radionuclide migration in fissured crystalline rock, data from experiments carried out under well defined conditions are required.

Our laboratory studies are focused on the transport of radionuclides in single natural fissures and the migration of the moderately sorbed Cs^{+} and Sr^{2+} ions are discussed in a previous report (1). The present report deals with the transport of Eu and the actinides Np and Pu.

EXPERIMENTAL

Flow systems: The rocks used in this study are granitic drillcores taken from Stripa mine at a depth of 360 m below ground. Each core used has a natural fissure running parallell to the axis. The cylindrical surfaces of the drillcores were sealed with a coat of urethane laquer to prevent any water to leave the rock except through the outlet end of the fissure. The granitic cylinders were thereafter mounted between plexiglas end-plates containing shallow in- and outlet channels slightly wider than the fissures (figure 1). Artificial groundwater was pumped for 2-3 days through the fissure to be used to preequilibrate the fissure surface. To characterize the waterflow artificial ground water containing a non-sorbing tracer was fed to

the inlet channel by a peristaltic pump (Istmatec IP-4) ensuring a steady flow through the fissure. Flushing water was simultaneously fed by the same pump through the outlet channel to reduce the time delay due to the channel volume. The effluent was continuously fed to a fraction collector for analysis of the tracer concentrations. The tracer was added as a pulse of suitable duration. The radionuclides studied were fed into the fissure by the same technique. After several hundred fissure volumes of water had been pumped through the fissure the rock cylinder was opened and the tracer distribution on the fissure surface was measured.

Solutions: All solutions were prepared using artificial ground water synthesized to represent the natural water in contact with the granite rock. The water composition is given in table 1 below. In all experiments the water used was deoxygenated by N_2 purging and the actinide experiments were carried out in a glove box with N_2 atmosphere. To characterize the water flow a lignosulphonate ion (mol wt $\sim$ 24 000) was used. This ion can be conveniently analyzed and do not sorb on the fissure surface. Tracer solutions of ^{152}Eu (Amersham), ^{235}Np and ^{237}Pu (Harwell) were prepared by diluting aliquots of acid (0.1-1 M HCl) stock solutions. The tracer concentrations used were ^{152}Eu ($5 \cdot 10^{-8}$ - $2 \cdot 10^{-7}$ mol$\cdot$dm^{-3}); ^{235}Np ($1 \cdot 10^{-9}$ mol$\cdot$dm^{-3}); ^{237}Pu($1.4 \cdot 10^{-10}$ mol$\cdot$dm^{-3}). The decay characteristics of the nuclides and measured radiation are given in table 2 below.

Tracer concentration measurements: The lignosulphonate ion displays a strong optical adsorption band with maximum at 280 nm ($\varepsilon \sim 3 \cdot 10^5$) and the LS^- concentration was therefore measured spectrophotometric at this wavelength. The ^{152}Eu, ^{235}Np and ^{237}Pu concentrations were determined from measurements of the activity using a (2" x 2") NaI well type detector.

The tracer activity on the fissure surfaces was measured with a (2" x 2")NaI planar detector fitted with a 0.6 cm^2 lead coli-

mator (figure 2). The detectors were connected to a computerized 256 channel pulse height analyzer.

Distribution coefficient measurements: Crushed granite was washed with ground water solution. The suspension was thereafter filtered through a 0.45 μm pore size Millipore filter and the solid material dried at 105°C. Known amounts of the dried crushed granite were suspended in ^{152}Eu solutions for 24 h. The suspensions were filtered through 0.45 μm pore size filters and the amount of ^{152}Eu in the granite and filtered solutions determined by γ-counting. The ^{152}Eu distribution coefficient was calculated using the equation

$$K_d = \frac{V}{W} \cdot R_S/R_L$$

where V = volume of ^{152}Eu solution
W = weight of crushed granite
R_S = net count rate of granite
R_L = net count rate of filtered solution.

EXPERIMENTAL RESULTS

To characterize the water flow non-interacting tracers are required. A number of assumed water true tracers normally used for this purpose were tested. Break through curves for some of the tracers tested and the concentration ratios C_{out}/C_{in} at $t = 10 \cdot t_{0.5}$ are depicted in figures 3, 4. The experiments gave with one exception near identical break through curves for all the tracers tested. As seen from figure 4 the ^{131}I concentration only reached the expected full value after a long delay. We have not investigated the reason for this effect any further but used NaLS in the present study.

^{152}Eu: In some earlier experiments it was found that a few per cent of the ^{152}Eu activity was transported through the fissure with the same velocity as water. The same phenomenon was observed in experiments with 2 cm^3 5 cm long columns filled with

crushed granite and 200-400 mesh H^+ saturated Ag-50 ion exchanger resin. On filtering the ^{152}Eu solution through a 0.21 μm filter the amount transported momentarily through the fissures could be very much reduced. To study the effect of the fraction of ^{152}Eu carried by particulates on the sorption on fissure surface experiments with and without 0.2 μm filter were carried out. Figures 5, 6 show eluate data for two experiments carried out with and without a 0.21 μm filter between the tracer solution reservoir and the inlet channel. The experiments were run simultaneously and the tracer solution fed from the same reservoir. The ^{152}Eu distribution on the fissure surfaces of the drill cores used in these experiments are depicted in figures 7, 8. Before opening the drill core ∿ 400 fissure volumes of ground water had been pumped through the fissure following a 15 minutes long pulse of tracer solution. The detection limit is ∿ 5cpm. In the batch adsorption experiments with 25, 50 and 100 mg crushed granite suspended in 25 ml solution the distribution coefficient was found to be $(1.4 \pm 0.2) \cdot 10^3$ cm^3/g.

^{235}Np: Data from corresponding experiments with ^{235}Np are shown in figures 9, 10. As seen the ^{235}Np activity is only retarded a factor 3-4. No ^{235}Np was found on the fissure surfaces on opening the drill core.

^{237}Pu: No ^{237}Pu was detected in the eluate. The distribution of ^{237}Pu on the fissure surface after 2 400 fissure volumes of ground water had been pumped through the drill core following the pulse of tracer solution is depicted in figure 11. 40% of the ^{237}Pu was found on the surface of the inlet channel and 60% on the fissure surface within 2 mm distance from the inlet channel.

DISCUSSION

When a radionuclide transported by water through a fissure reacts with the surface of the fissure the radionuclide will be retarded relative to the water. In the simplest case of a fast reversible reaction and linear equilibrium the retardation factor R is given by the equation

$$R = \frac{U_w}{U_{rn}} = 1 + a \cdot K_a$$

where U_{rn}, U_w is the velocity of radionuclide and water respectively,
$a = a_f/V_f$ is the ratio of fissure surface area and volume, and
K_a cm^3/cm^2 is the surface distribution coefficient.

The radionuclide retardation R was calculated using the equation

$$R = (V_w/V_f) \cdot l/\bar{l}$$

where V_w is the total volume water pumped through the fissure. l is the fissure length and $\bar{l}$ the mean distance travelled by the radionuclide (from radionuclide distribution on fissure walls).

The K_a values calculated from the flow experiments are based on the geometrical fissure area, i e the surface roughness is not taken into account. Most of the published distribution coefficients (K_d) have been determined in batch experiments with crushed granite, and thereby calculated on weight and not surface area basis. The ratio of the distribution coefficients is given by the equation

$$K_a = K_d \cdot \rho/a$$

where ρ is the density (g/cm^3) and a the surface/volume ratio of the granite.

Thus to compare the K_a values obtained from flow experiments with K_d values from batch equilibrium experiments knowledge of the exposed surface areas of the fissures and crushed granite are required.

A very approximate comparison can, however, be made if it is assumed that the exposed surface/geometric surface ratio is equal. The crushed granite is assumed to consist of spherical beads and the surface area/volume ratio is thus 6/d, where d is the bead diameter. The transport parameters and K_d-values calculated on basis of these assumptions are given in tables 3 and 4 respectively. For comparison K_d values for the radionuclides ^{235}Np and ^{237}Pu obtained by Allard (4) are given in table 4. The K_d-values calculated from the flow experiments are somewhat higher than the K_d values obtained in batch experiments, but in view of the uncertainties involved the agreement is satisfactory. From the K_d-values obtained it can be concluded that the radionuclides studied were transported in the following oxidation states (5), Eu(III), Pu(IV), Np(V).

In our experiments a few per cent of the ^{152}Eu and ^{235}Np was carried with the water flow on particulates with d > 0.21 μm. This effect may partly be due to precipitation and partly to adsorption on particulates formed in the synthetic ground water.

ACKNOWLEDGEMENTS

The experimental help by P-I Olsson, I Johansson and S O Engman is gratefully acknowledged.

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Table 1: Composition of the artificial ground water used in experiments (ref 2).

Substance	Concentration	
	$mol \cdot dm^{-3}$	ppm
HCO_3^-	$2.014 \cdot 10^{-3}$	123
H_4SiO_4	$2.056 \cdot 10^{-4}$	12
SO_4^{2-}	$1.000 \cdot 10^{-4}$	9.6
Cl^-	$1.973 \cdot 10^{-3}$	70
Ca^{2+}	$4.477 \cdot 10^{-4}$	1.8
Mg^{2+}	$1.774 \cdot 10^{-4}$	4.3
K^+	$1.000 \cdot 10^{-4}$	3.9
Na^+	$2.836 \cdot 10^{-3}$	65

Table 2: Decay characteristics of the radionuclides used (ref 3).

Nuclide	Half-Life	Mode of decay	Measured radiations
^{152}Eu	12.4y	EC, β^-	γ
^{235}Np	410	EC, α	U x-rays
^{237}Pu	45.6d	EC, α	Np x-rays

Table 3: Experimental transport parameters calculated from break through curves and radionuclide distribution on fissure surfaces.

Radionuclide	Fissure volume (V_f) cm^3	Fissure[a] surface (a_f) cm^2	a_f/V_f cm^{-1}	Radionuclide[b] retardation $R = U_w/U_{rn}$
^{152}Eu	1.2	64	53	1067 3000
^{235}Np	1.35	64	47.5	4.2
^{237}Pu	0.6	135	225	$> 2 \cdot 10^5$

a) Geometric area.

b) Velocity of water (U_w) and radionuclide (U_{rn}) respectively.

Table 4: Distribution coefficients calculated from break through curves and radionuclide distribution on fissure surfaces. Distribution coefficients from batch equilibrium experiments.

Radionuclide	Particle size fraction cm	K_d (equil) cm^3/g	K_a[a] cm^3/cm^2	K_d[a] cm^3/g
^{152}Eu	0.01-0.0012	$1.4 \cdot 10^3$	20.3	$4.2 \cdot 10^3$ $1.17 \cdot 10^4$
^{235}Np	0.0044-0.0063	30-70[b]	0.088	37
^{237}Pu	0.0044-0.0063	$2 \cdot 10^3$-10^5[b]	0>820	$>3.4 \cdot 10^5$

a) Calculated during geometric surface areas, using the equation $K_a = K_d \cdot \rho/a$.

b) Data taken from reference 4.

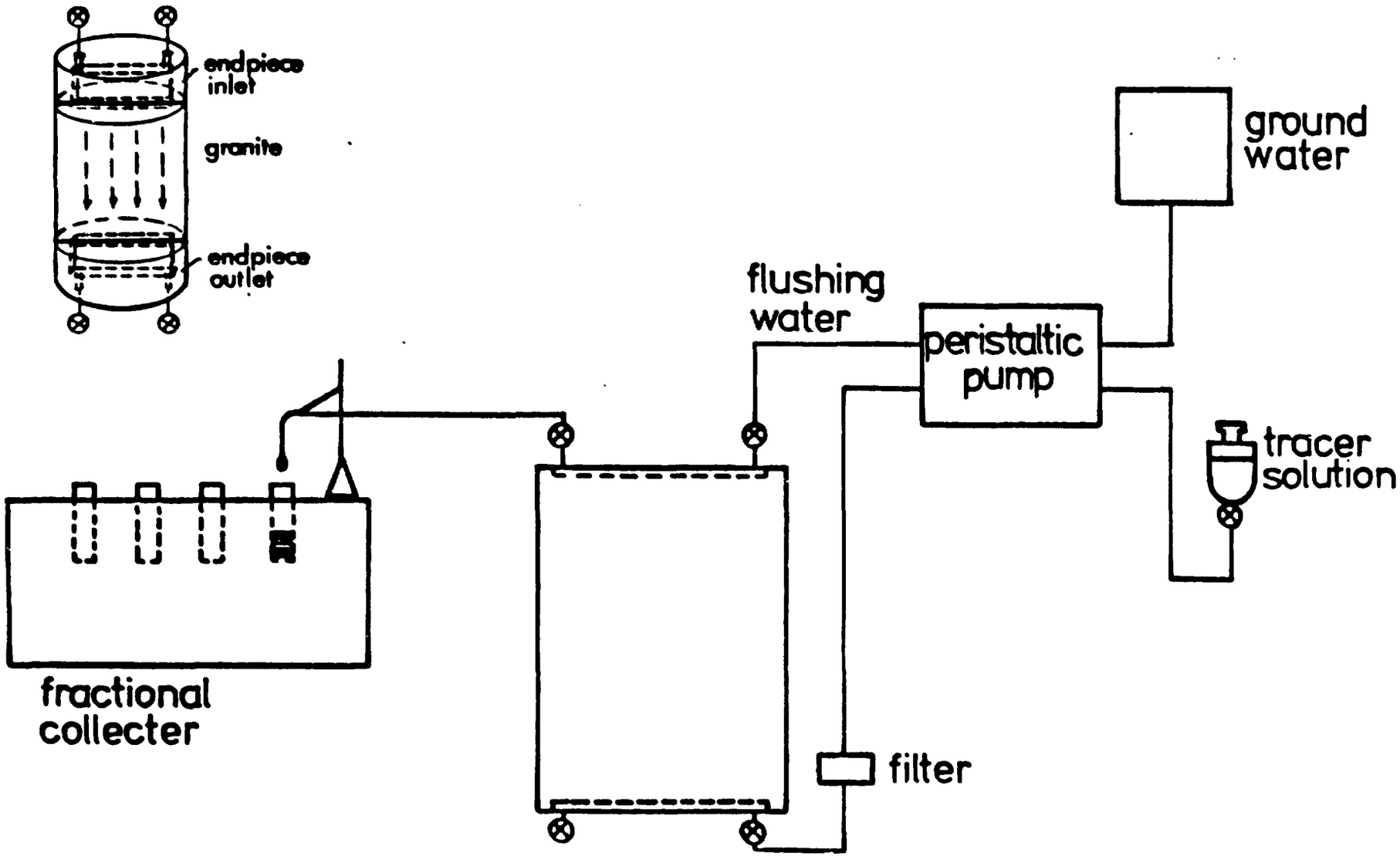

Figure 1.
Experimental set up.

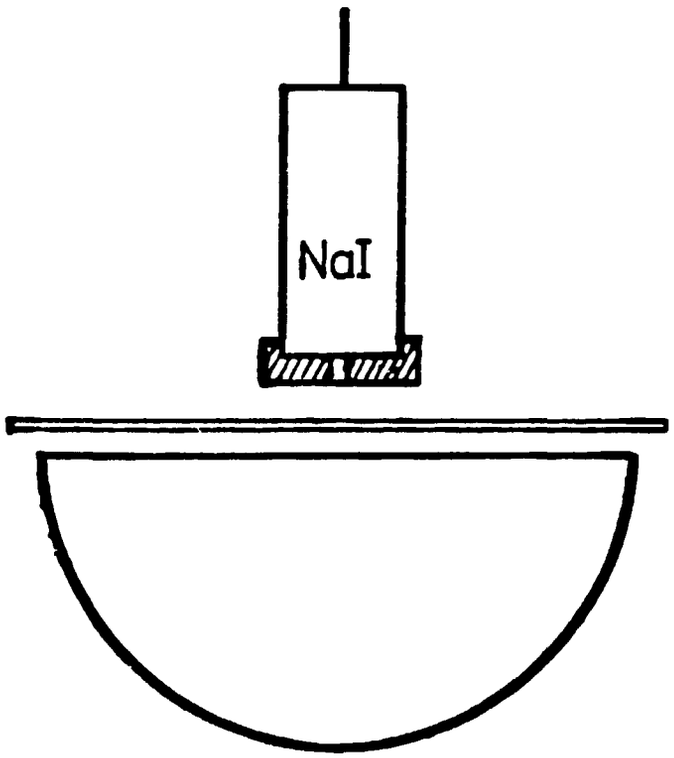

Figure 2.
Detector set up for scanning the fissure surfaces. Collimator area 0.6 cm^2.

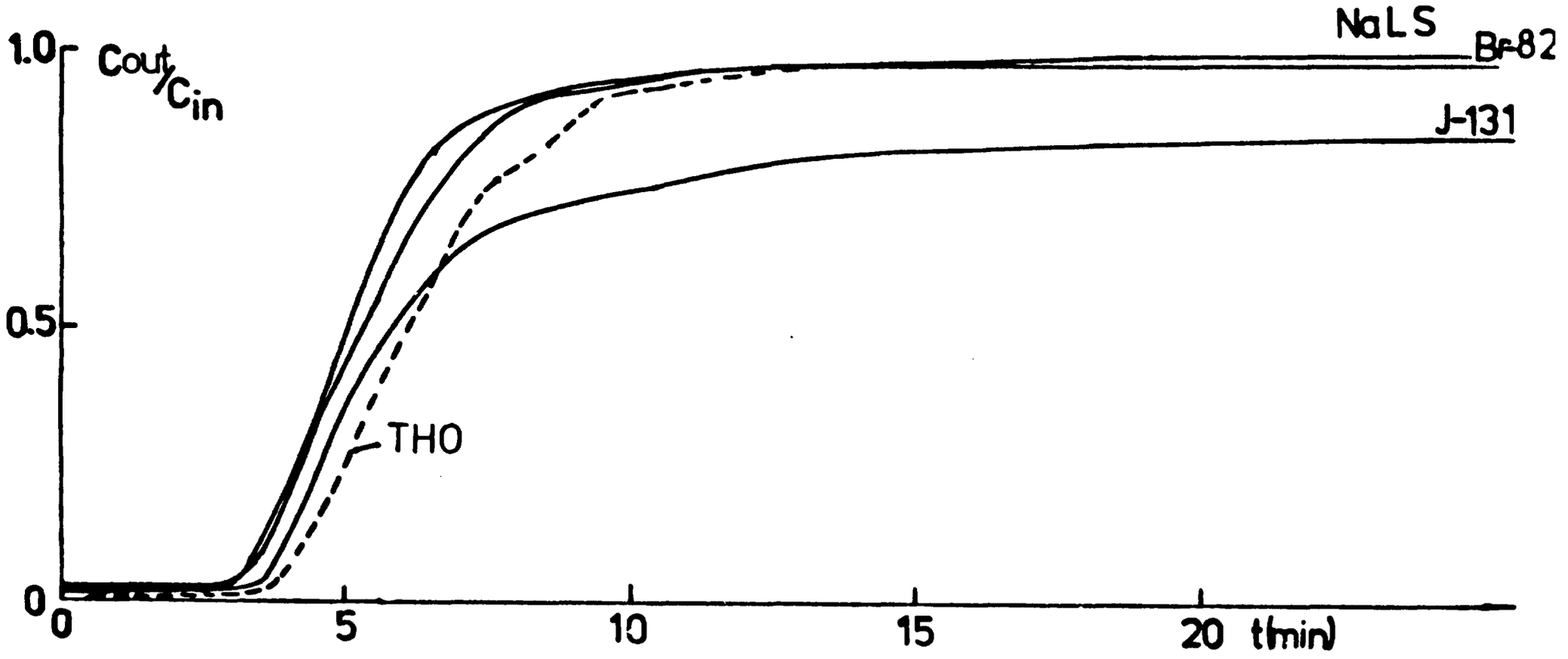

Figure 3.

Experimental break through curves for some tracers, assumed to be non-sorbing.

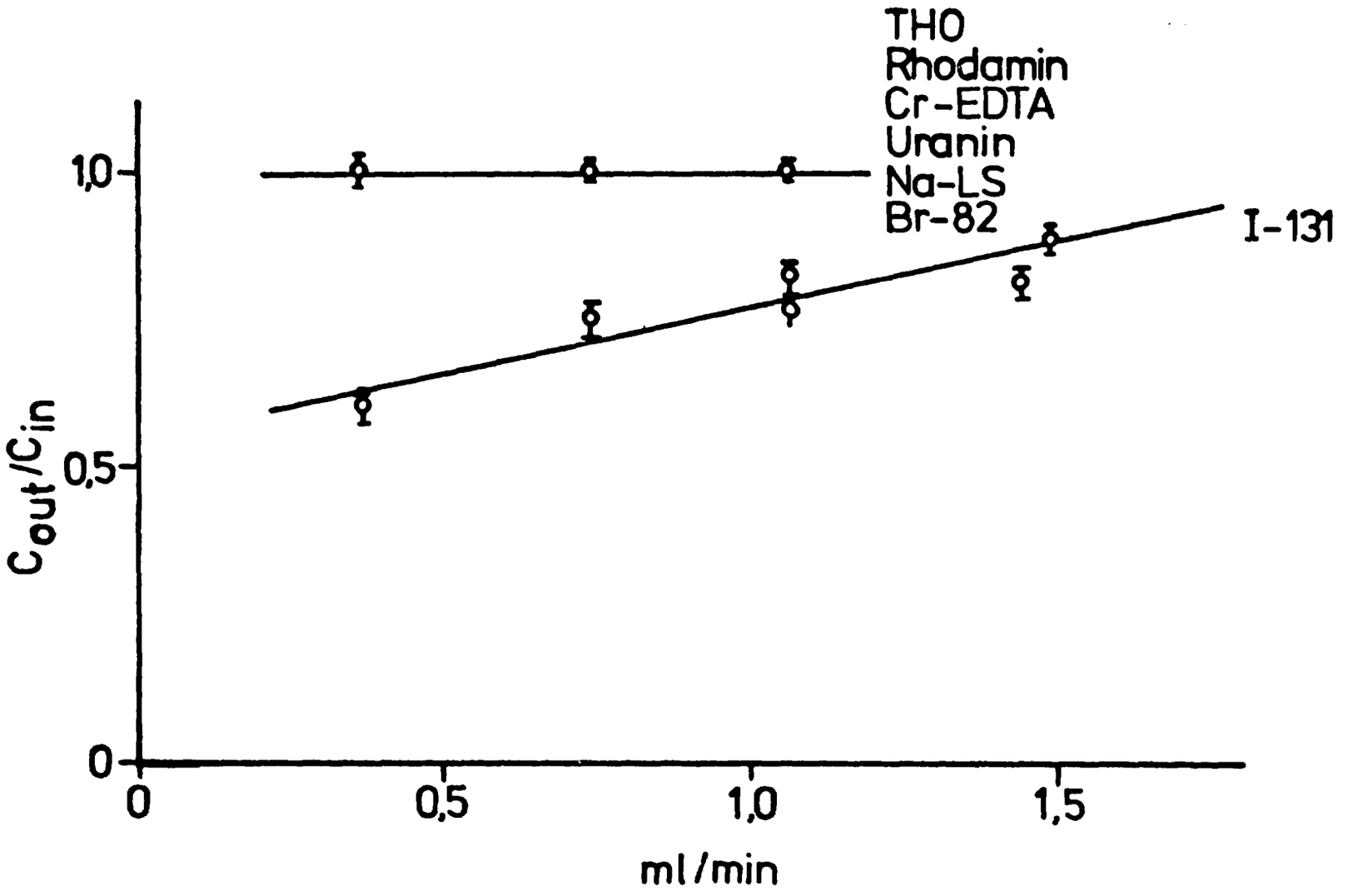

Figure 4.

Relative concentrations of some tracers assumed to be non-sorbing at $t = 10 \times t_{0.5}$.

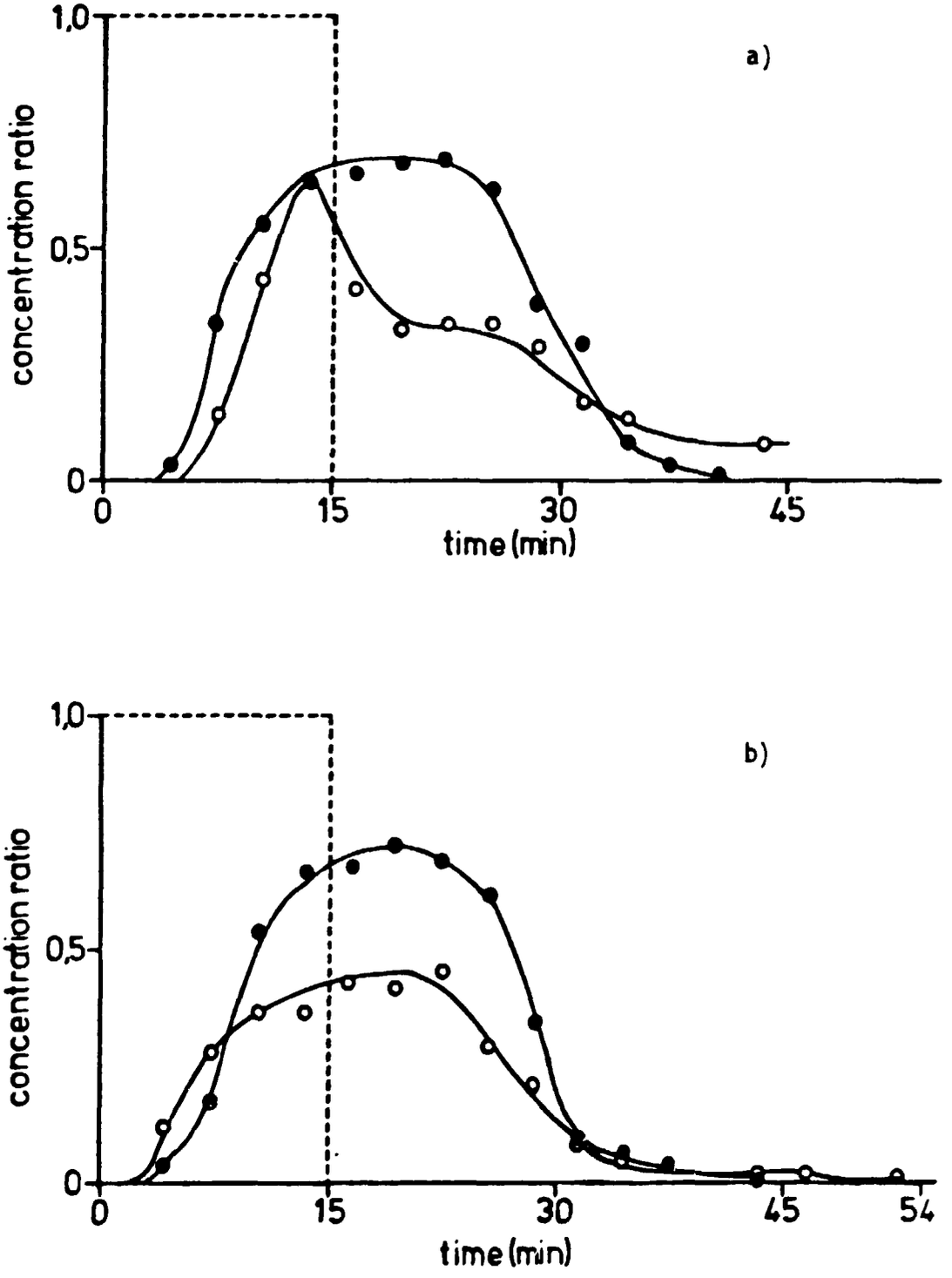

Figure 5.

Tracer concentrations in eluate. Drill core: ϕ 40 mm; l = 80 mm. Tracer pulse: 15 min. Water flow: 0.1 cm^3/min.

a) · LS^- C_{out}/C_{in}
o ^{152}Eu $(C_{out}/C_{in}) \times 10^2$
0.21 μm filter

b) · LS^- C_{out}/C_{in}
o ^{152}Eu $(C_{out}/C_{in}) \times 10$
no filter

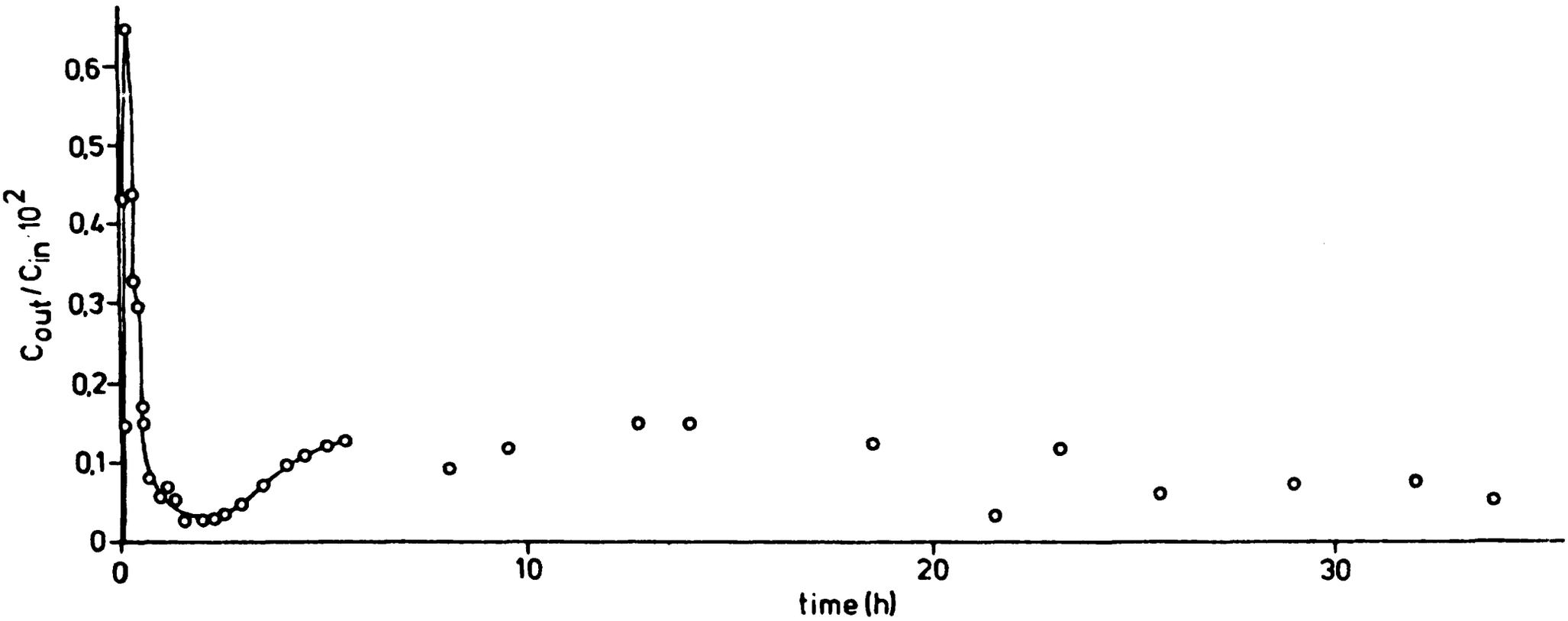

Figure 6.
^{152}Eu concentration in eluate vs time (same experiment as in figure 5a).

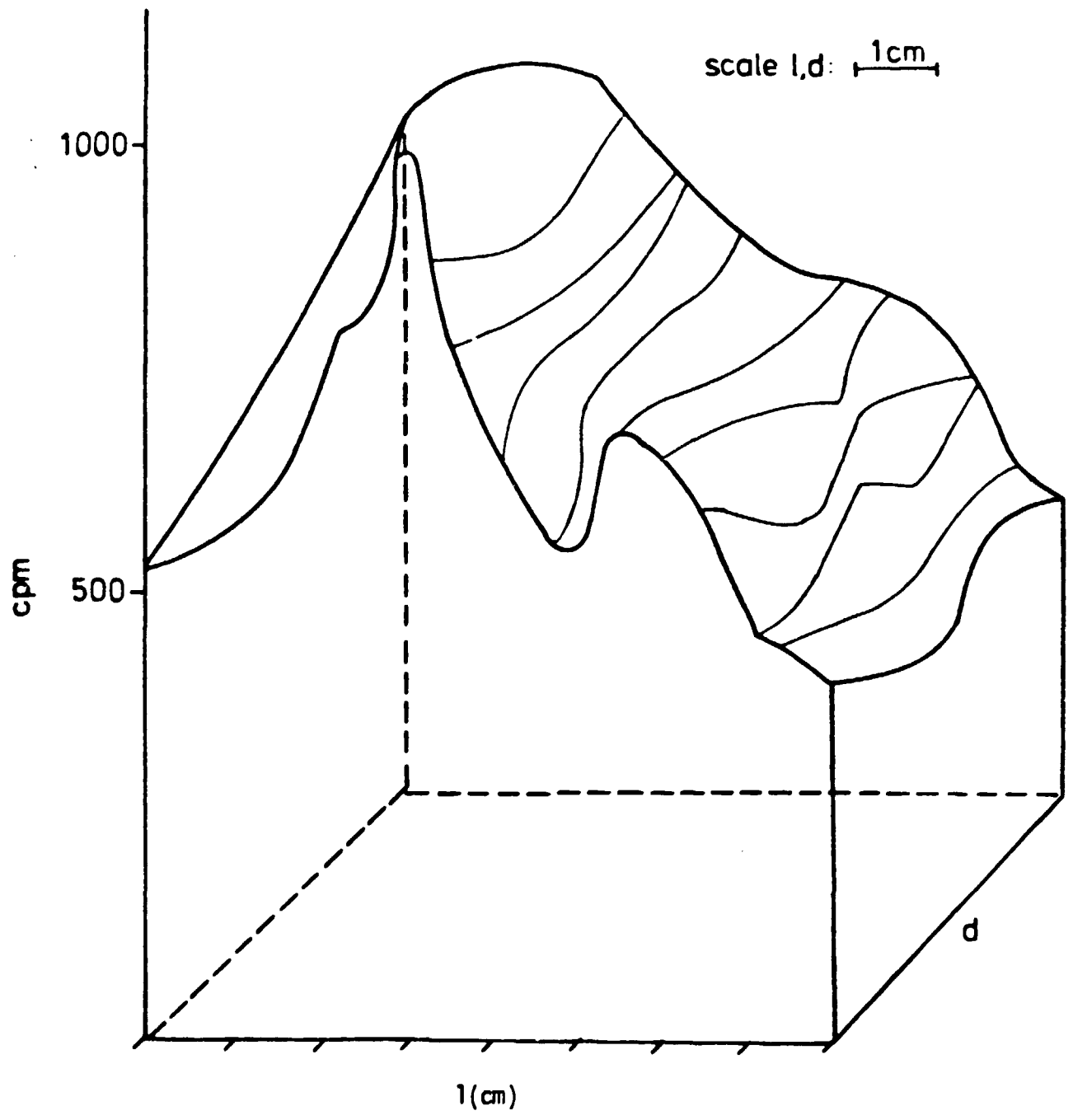

Figure 7.

^{152}Eu distribution on fissure surface 77.5 h after onset of tracer flow through fissure. Φ = 40 mm, l = 80 mm, water flow 0.1 cm^3/min, 0.21 µm filter. (Flow data plotted in figures 5a, 6).

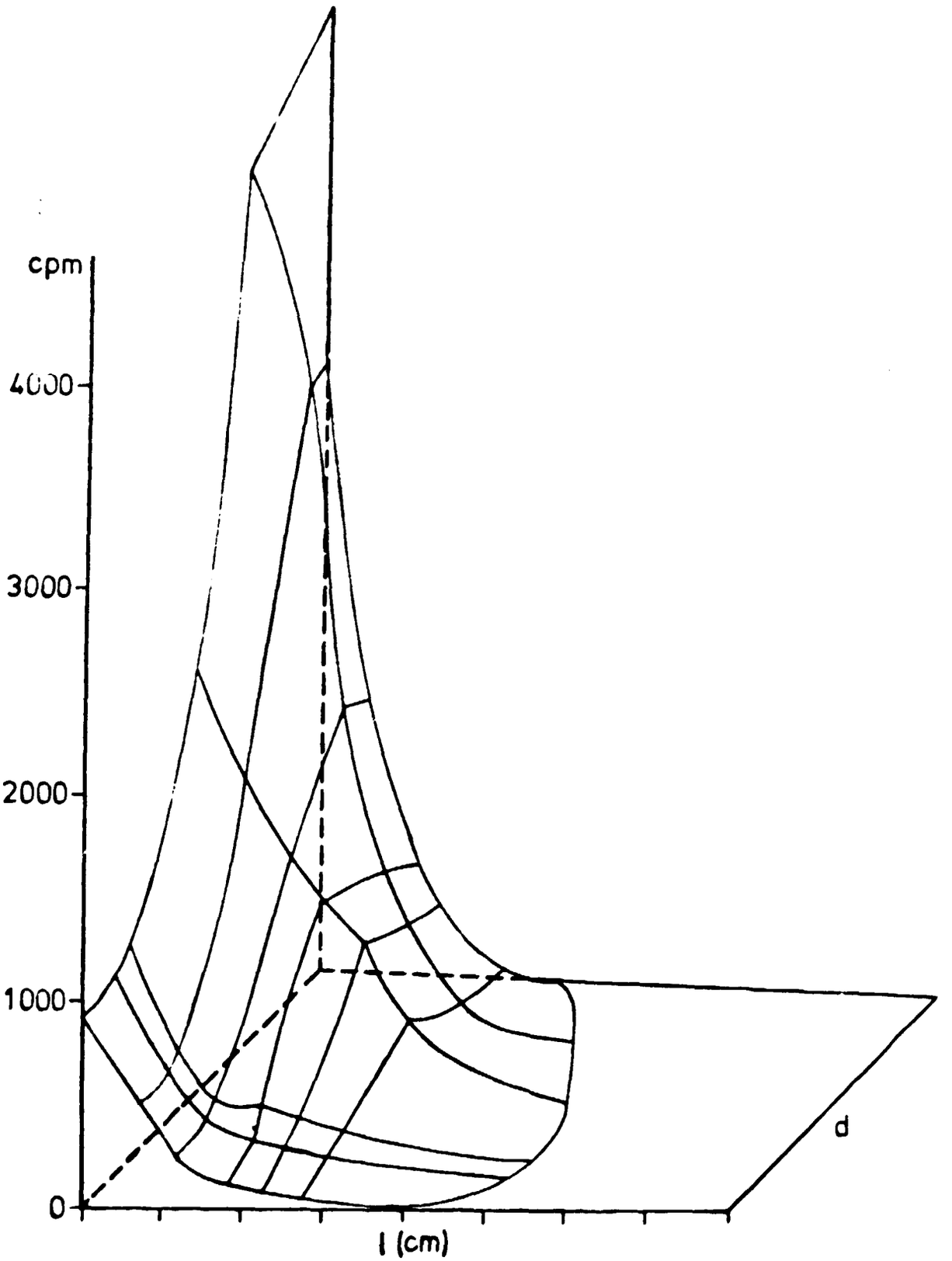

Figure 8.

^{152}Eu distribution on fissure surface 77,5 h after onset of tracer flow through fissure. ϕ = 40 mm, l = 80 mm, water flow 0.1 cm^3/min. No filter. Flow data plotted in figure 5b.

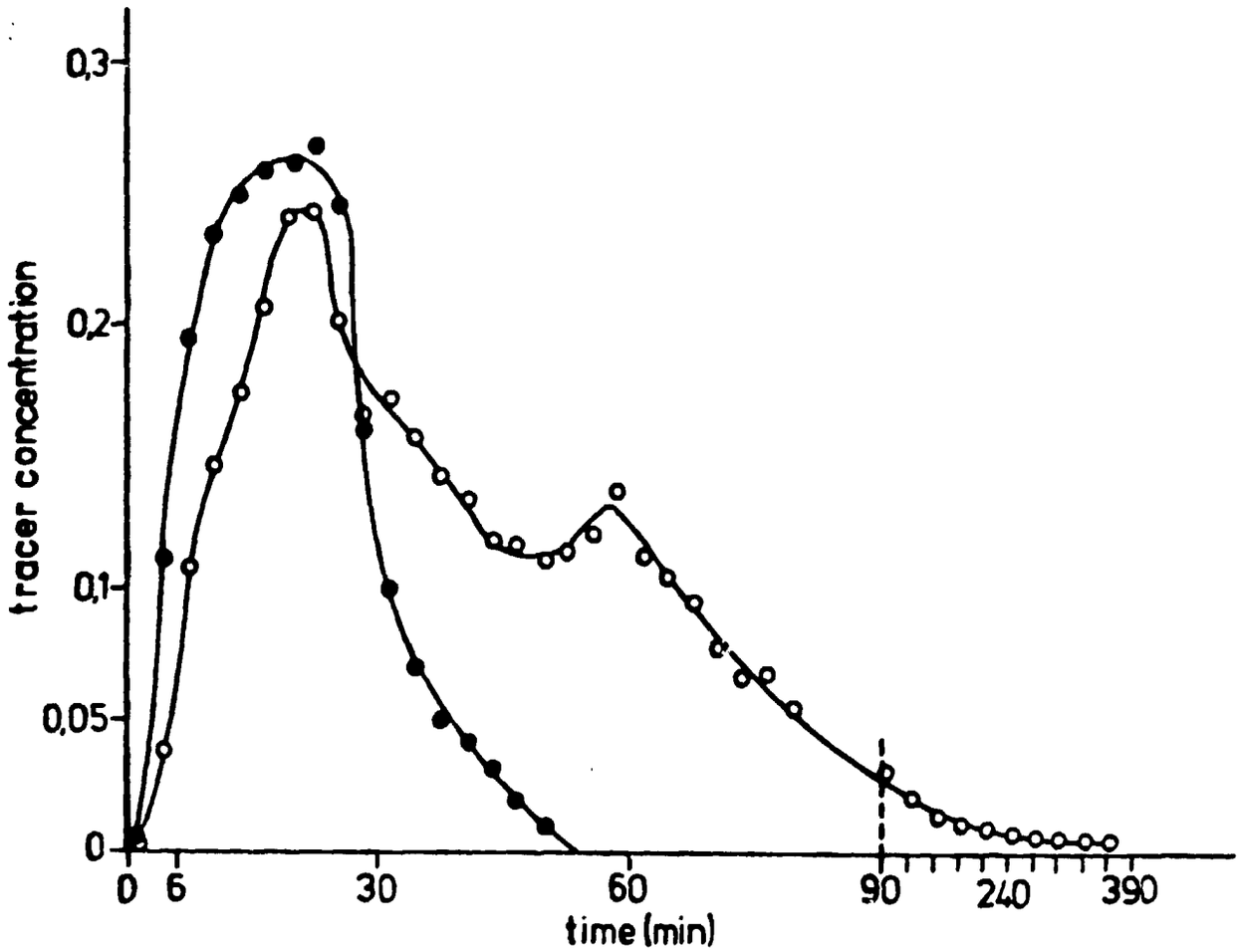

Figure 9.

Tracer concentration in eluate vs time.

ϕ = 40 mm, l = 80 mm, water flow 0.1 cm^3/min, no filter.

• LS^- Absorbance at 280 nm

o ^{235}Np C_{out}/C_{in}

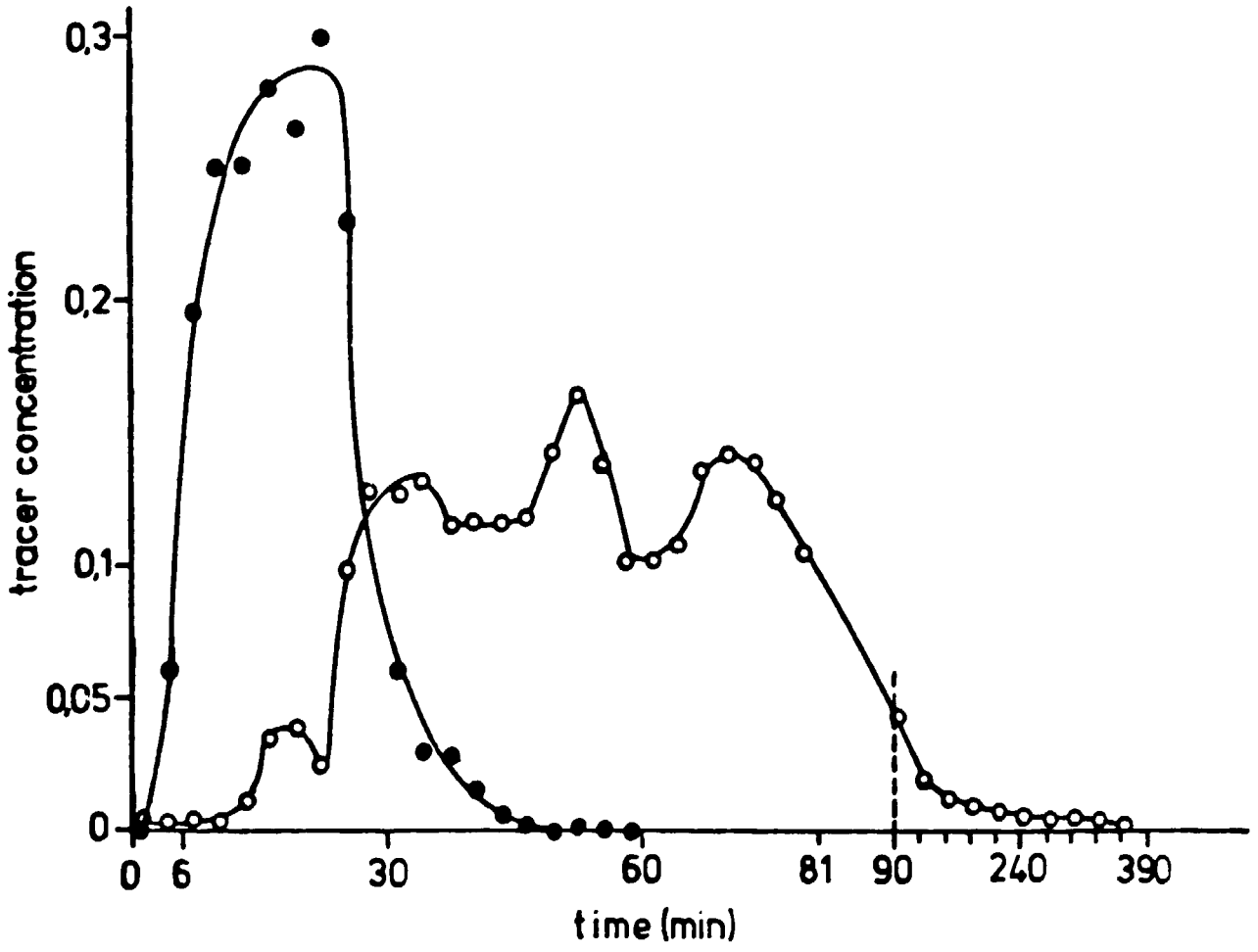

Figure 10.

Tracer concentration in eluate vs time.

ϕ = 40 mm, l = 80 mm, water flow 0.1 cm^3/min,

0.21 µm filter.

· LS^- Absorbance at 280 nm

o ^{235}Np C_{out}/C_{in}

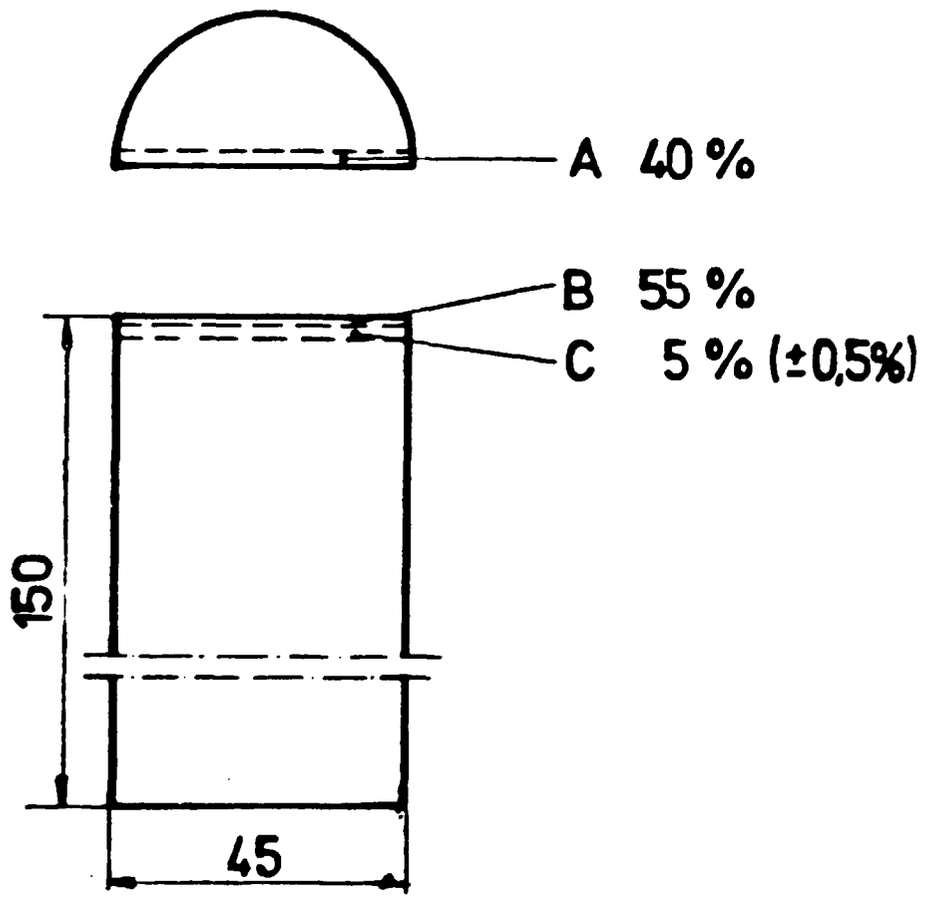

Figure 11.

^{237}Pu distribution on fissure surface, 10 days after onset of tracer flow through fissure.

ϕ = 45 mm, l = 150 mm, water flow 0.1 cm^3/min. Fissure volume 0.6 cm^2.

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