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Radionuclide transport in a single fissure
A laboratory study of Am, Np and Tc

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RADIONUCLIDE TRANSPORT IN A SINGLE FISSURE

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CONTENTS

SUMMARY

Radionuclide migration has been studied in natural fissures running parallel to the axes of granitic drill cores. A short pulse of radionuclide solution was injected at one end of the fissure and the temporal change in radionuclide concentration of the eluate measured.

At the end of each experiment the fissure was opened and the radionuclide distribution on the fissure surfaces measured. The retardation of $^{241}Am(III)$ at pH 8.2 as well as the variation in $^{235}Np(V)$ retardation with pH are found to be in good agreement with K_d-values obtained in batch experiments.

The reduction of (TcO_4^-) to Tc(IV) leads as expected to increasing retardation.

INTRODUCTION

In fissured crystalline rock the radionuclides carried by the water flowing through the fissures will interact in various ways with the rock. The radionuclides may be strongly retarded by sorption, ion exchange, complexation and hydrolysis and may also diffuse into the microfissures of the rock matrix.

For multivalent elements such as technetium and the actinides the chemical conditions eg redox potential, pH and concentration of complexing agents are of outmost importance.

For the understanding and possible prediction of radionuclide migration in natural fissures data from experiments carried out under well defined conditions are needed.

In previous reports (1-3) we discussed the transport of Cs^{+}, Sr^{2+}, Eu^{3+}, Pu(IV) and Np(V). The present study deals with Tc(IV), Tc(VII), Am(III) and the effect of pH on the migration of Np(V).

EXPERIMENTAL

Flow systems: The rock used in our studies are granitic drill cores taken from Stripa mine at a depth of 360 m below ground

level. Each core used has a natural fissure running parallel to the axis. The cylindrical surfaces of the drill cores were sealed with a coat of urethane lacquer 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 fissure (figure 1).

Prior to any tracer experiment synthetic ground water was pumped through the fissure by a peristaltic pump (Istmatec IP-4) for several days to equilibrate the fissure surfaces. To characterize the water flow a solution of a nonsorbing tracer in ground water was pumped through the fissure and flushing water 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 concentration. The nonsorbing tracer was added as a puls of suitable duration (normally 15 min) and the radionuclides studied were fed into the fissure by the same technique. The radionuclide was eluated by continuously pumping water through the fissure.

After several hundred fissure volumes of water hade been pumped through the fissure the rock cylinder was opened and the tracer distribution on the fissure surfaces measured.

The experiments were carried out in a glove box. When reducing conditions were required the glove box was evacuated and filled with Ar-gas (Aga SR-quality).

Solutions: The radionuclides used were ^{241}Am (Amersham), ^{99}Tc (Amersham) and ^{235}Np (Harwell) received in acid solutions. ^{99m}Tc was recovered from a ^{99}Mo generator (Kjeller). The oxic Tc and Am solutions were prepared using artificial ground water synthesized to represent the natural water in contact the granitic rock (the composition is given in table 1). Tracer solutions were prepared by diluting aliquotes of stock solutions. The ^{235}Np solutions were prepared using distilled water. In all cases pH was adjusted by NaOH or HCl.

The experiment with Tc(IV) was carried out with a tracer solution prepared by adding $^{99m}TcO_4^-$ and $^{99}TcO_4^-$ to 250 cm^3 of an Ar-purged aqueous solution of $NaHCO_3$ (1680 $mg \cdot dm^{-3}$), Na_2CO_3 (76 $mg \cdot dm^{-3}$), KCl (10 $mg \cdot dm^{-3}$). pH and Eh were stabilized by addition of $CaCO_3$ (10 mg tot) and $FeSO_4$ (88 $mg \cdot dm^{-3}$) respectively. The eluation was carried out with Ar-purged synthetic ground water (see table 1) containing 88 $mg \cdot dm^{-3}$ $FeSO_4$.

Tracer concentration measurements: The characteristic properties of the tracers used are given in table 2 below. The lignosulphonate ion (LS^-) displays a strong optical absorption band

around 280 nm ($\varepsilon \sim 3 \cdot 10^5$) and the LS^- concentration was therefore measured spectrophotometrically at this wavelength.

The ^{235}Np, ^{99m}Tc and ^{241}Am concentrations in the effluent were determined from measurements of the activity using a (2"x2")NaI well type of detector. In one experiment the ^{99}Tc concentration in the eluate was measured by adding ~0.1 cm^{-3} of the eluate to 2 cm^{-3} Aquasol and measuring the light intensity in a luminometer (LKB).

Tracer distribution measurements: The tracer distributions on the fissure surfaces were measured with a (2"x2")NaI planar detector (^{241}Am, ^{235}Np) or a GM-tube (^{99}Tc) fitted with lead collimators.

EXPERIMENTAL RESULTS

The experimental results are plotted in figures 2-10 and further details are given in table 3 below.

Am(III): The experiment was carried out under oxic conditions. A small fraction of the total ^{241}Am activity was transported through the fissure with the same velocity as water (figure 2). The same phenomenon was observed in earlier experiments with Eu, Np and Pu and has been ascribed to sorption on particulates in the artificial ground water (3).

The ^{241}Am distribution on the fissure surfaces is depicted in figure 3. The distribution shows a similar pattern as reported earlier for ^{152}Eu (3) i.e. a decrease in surface activity with distance from inlet both along the inlet channel and fissure depth.

Tc: The flow data from ^{99}Tc transport in air saturated solution are plotted in figure 4. As seen the transport rate corresponds to the water flow rate.

On reduction of TcO_4^- only a small fraction of the total ^{99m}Tc activity in the tracer pulse passed through the fissure with the same velocity as water (figure 5). The ^{99}Tc distribution on the fissure surfaces 24 h after onset of the tracer pulse is depicted in figure 6.

Np: The concentration in the eluate from experiments at pH 6, 8 and 9 are plotted in figures 7-8.

At pH 6 the ^{235}Np was transported through the fissure with the same velocity as water and at pH 8 the retardation is about 2. At pH 9 a small fraction of the total ^{235}Np activity is transported through the fissure with only a slight delay.

The ^{235}Np distribution on the fissure surfaces 6.5 h after onset of the tracer pulse at pH 9 is shown in figure 9. As seen the ^{235}Np activity is found within 3 cm distance from the inlet.

DISCUSSION

In the simplest case with a fast reversible sorption process the retardation R of a radionuclide relative to water, assuming no diffusion into the rock matrix, is given by the equation

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

U_{rn}, U_w are the velocities of the radionuclide and water respectively,

$a = a_f/V_f$ is the ratio of fissure surface area and fissure volume, and

K_a cm^3/cm^2 is the surface distribution coefficient.

The radionuclide retardation R can be calculated using the equation

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

where V_w is the total volume of water pumped through the fissure after the onset of the tracer pulse, l is the fissure length and $\bar{l}$ mean distance travelled by the radionuclide.

The R values calculated from the flow experiments are given in table 4 below. It ought to be emphasized that the calculations are based on geometrical fissure areas, i.e. the surface roughness is not taken into account. The comparison of K_a values,

calculated from the flow data according to the equation $R = 1 + a \cdot K_a$, with K_d values determined in batch experiments is based on the following assumptions.

The batch experiments have been carried out with crushed granite which is assumed to consist of spherical beads. The surface/volume ratio is thus 6/d where d is the bead diameter, and the ratio of the distribution coefficients is given by the equation

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

where ρ is the density ($g \cdot cm^{-3}$) and a the surface/volume ratio of the granite.

The K_d-values calculated from the flow data are given in table 5. As seen these are in good agreement with the K_d-data obtained for Am(III) and Np(V) by Allard et al (4). The K_a-values obtained for Np(V) are plotted vs pH in figure 10. The sharp increase in K_a with pH in the pH-range 8-9 clearly demonstrates the effect of hydrolysis, i.e. $NpO_2^+ + OH^- = NpO_2(OH)$ (5).

The Tc experiment carried out in reducing solution give a strong Tc retardation compared to the transport of TcO_4^-. The ^{99m}Tc is, however, found on the surface all along the fissure and may indicate that some oxidation of Tc(IV) has taken place.

ACKNOWLEDGEMENTS

The experimental work by S O Engman and I Johansson is gratefully acknowledged.

REFERENCES

1. Eriksen T E, Tähtinen P,
Utveckling av teknik för laboratoriemätning av radionukliders fördröjning och dispersion i bergsprickor.
Prav report 4.12 (1980).

2. Neretnieks I, Eriksen T E and Tähtinen P,
Tracer movement in a single fissure in granitic rock.
Some experimental results and their interpretation.
(Prav report 4.21)
Water resource research 1982, 18:4, 849.

3. Eriksen T E,
Radionuclide transport in a single fissure.
A laboratory study.
KBS report 83-01.

4. Allard B,
Sorption of actinides in granitic rock.
KBS report 82-21.

5. Allard B et al,
Sorption behaviour of well defined oxidation states.
KBS report 83-61.

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

Characteristics of tracers used.

Tracer	Halflife	Mode of decay	Measured
NaLS[A]			optical absorbance at 280 nm
mol wt 30.000			$\varepsilon \sim 3 \cdot 10^5$
^{99}Tc	2.1×10^5 y	β^-	β^-
^{99m}Tc	6 h	IT	γ
^{235}Np	410 d	α, EC	γ
^{241}Am	458 y	α	γ

[A] sodium-lignosulphonate

Table 3.

Description of flow experiments.

Radio-nuclide	Exp.cond.	Drill-core dimensions (mm)	Eluation[x)] time (h)	Fig.no.
^{241}Am	ox	ϕ=38, l=94	122,4	2.3
^{99}Tc	ox	ϕ=36, l=80	1.5	4
$^{99}Tc/^{99m}Tc$	red	ϕ=36.5, l=99	24	5.6
^{235}Np	ox, pH 6	ϕ=37, l=103.5	23	7
"	ox, pH 8	"	23.8	8
"	ox, pH 9	"	6.5	9

x) Tracer pulse length 15 min.

Table 4.

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

Radio-nuclide exp.cond.	Fissure volume $V_f(cm^3)$	Fissure surface [a] $a_f(cm^2)$	a_f/V_f cm^{-1}	Radionuclide [b] retardation $R=U_w/U_{rn}$
^{241}Am(ox)	1.5	71.4	47.6	~1350
^{99}Tc(ox)	1.1	57.6	52.4	1
^{99m}Tc(red)	1.74	72.3	41.5	~40
^{235}Np pH 6	1.62	76.6	47.3	1
pH 8	"	"	"	~2
pH 9	"	"	"	~300

a) Geometrical area.

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

Table 5.

Distribution coefficients calculated from break through curves and radionuclide distribution on fissure surfaces. Comparison with distribution coefficients from batch equilibrium experiments.

Radio-nuclide	Particle size fraction (cm)	K_d(equil) [b] cm^3/g	K_a [a] $cm^3 \cdot cm^{-2}$	K_d [a] $cm^3 \cdot g^{-1}$
^{241}Am	0.0044-0.0063	$(0.4\text{-}3) \cdot 10^4$	28.36	$1.2 \cdot 10^4$
^{99}Tc(ox)		0	0	0
^{99m}Tc(red)			~1	~420
^{235}Np(pH=6)	0.0044-0.0063	1-2	0	0
^{235}Np(pH=8)	0.0044-0.0063	~20	~0.042	~17
^{235}Np(pH=9)	0.0044-0.0063	$(0.6\text{-}1) \cdot 10^3$	~6.34	$\sim 2.7 \cdot 10^3$

a) Calculations based on geometric surface areas, using the equation

$K_a = K_d \cdot \rho / a$

b) Data taken from reference 4.

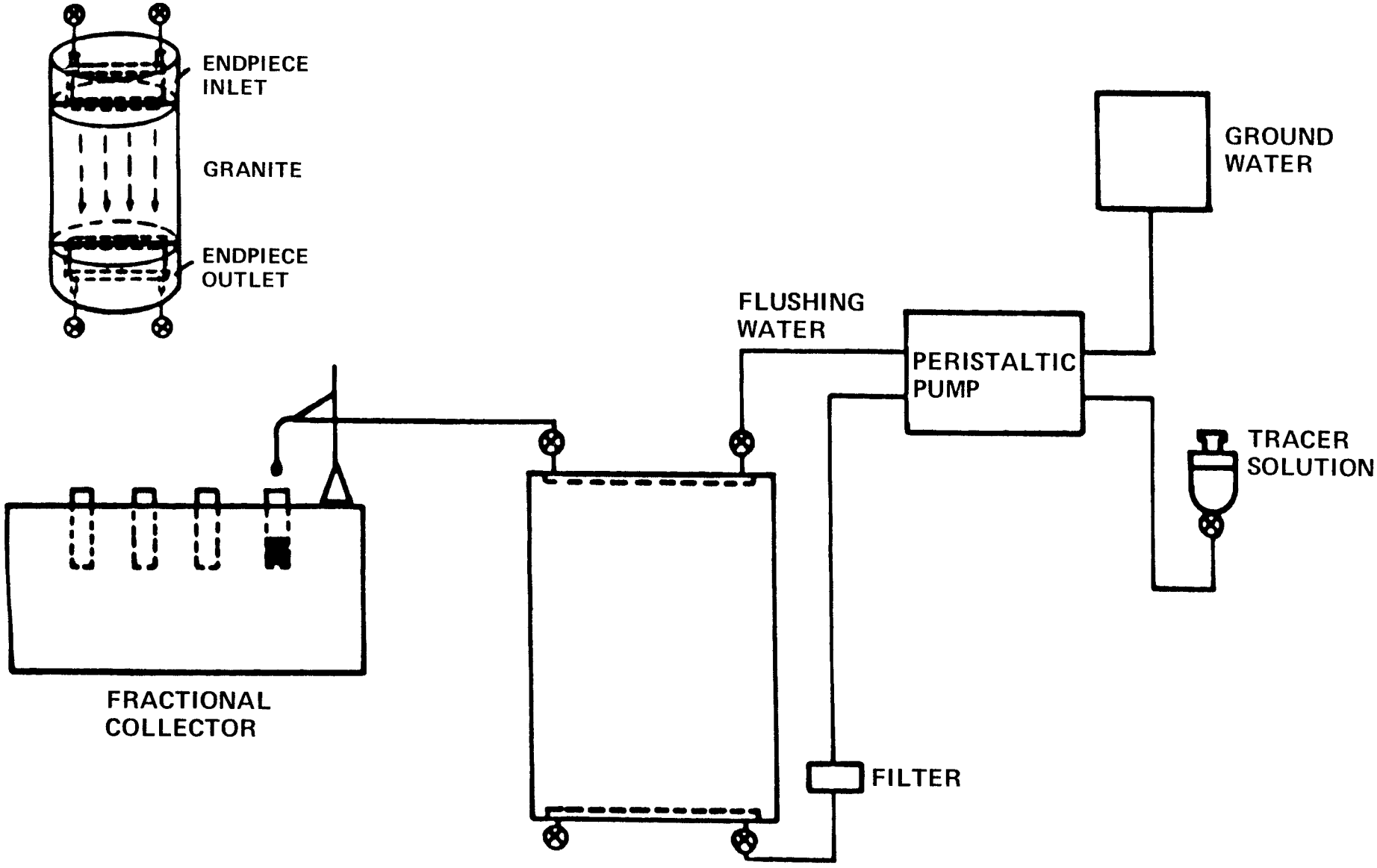


Figure 1.

Experimental set up.

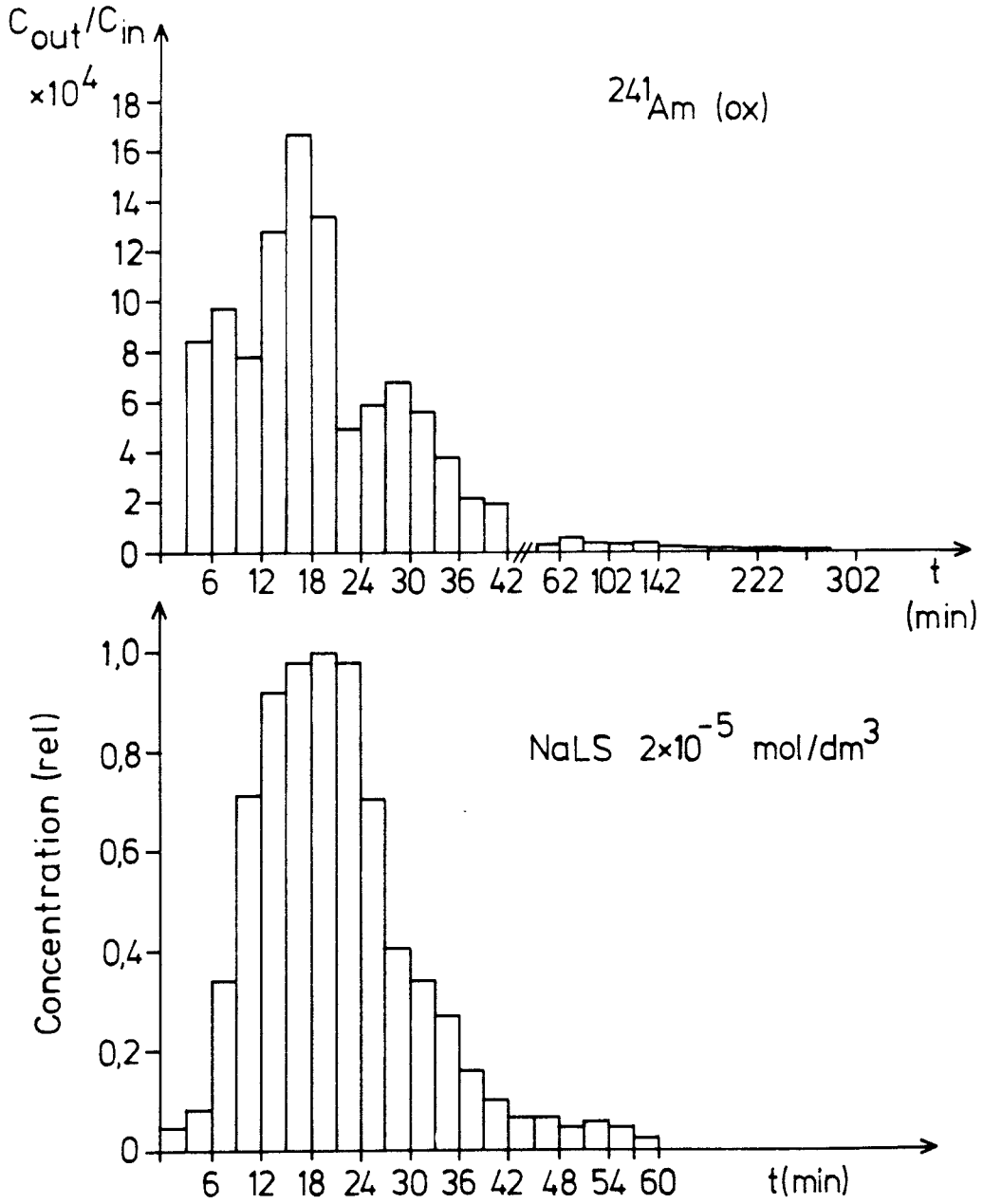
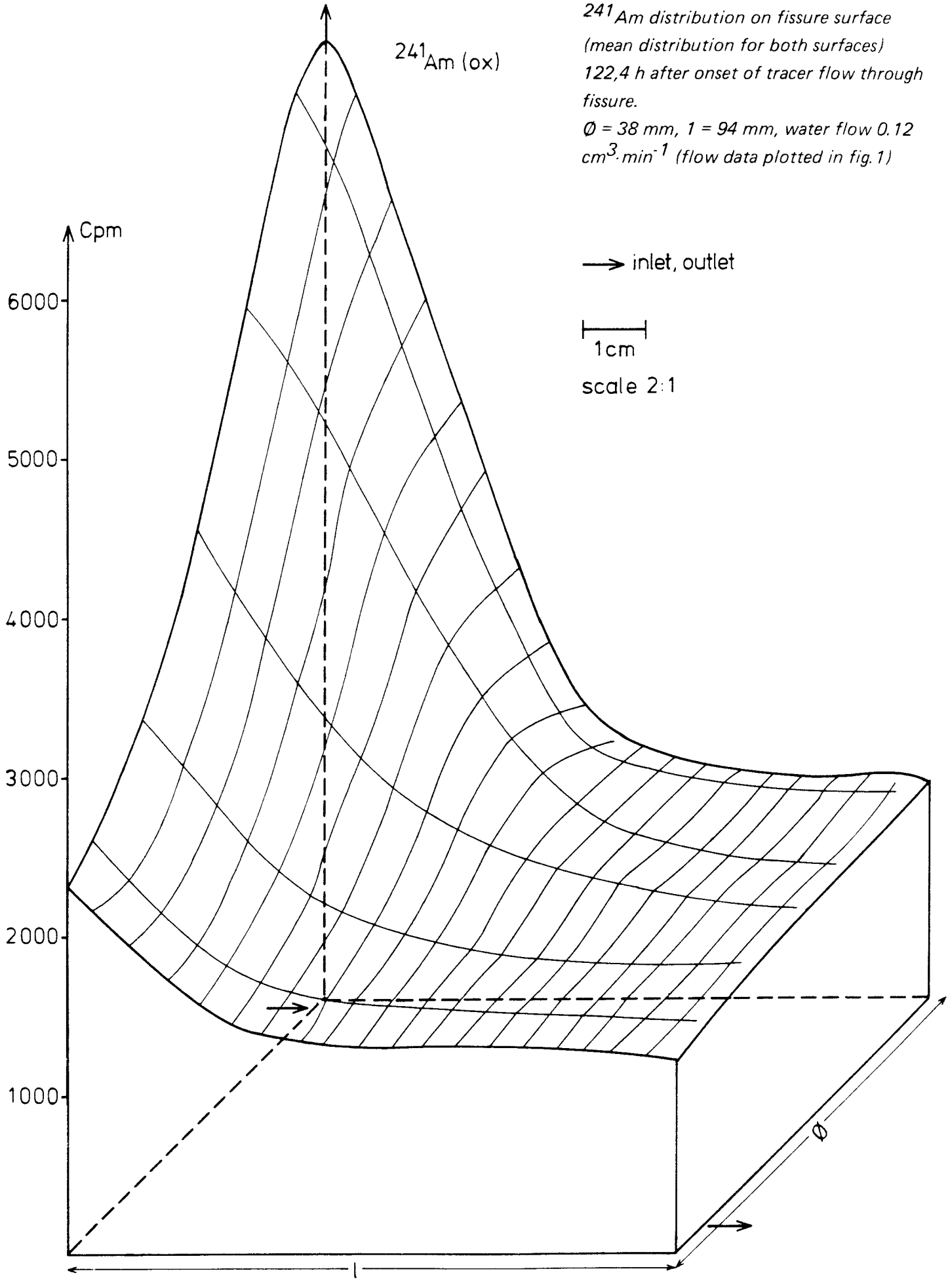


Figure 2.

Tracer concentration in eluate vs time.
Tracer pulse length 15 min.
Water flow 0.12 $cm^3 \cdot min^{-1}$.
Drill core Ø = 38 mm, l = 94 mm.

Figure 3.

^{241}Am distribution on fissure surface (mean distribution for both surfaces) 122,4 h after onset of tracer flow through fissure.
Ø = 38 mm, 1 = 94 mm, water flow 0.12 $cm^3 \cdot min^{-1}$ (flow data plotted in fig. 1)



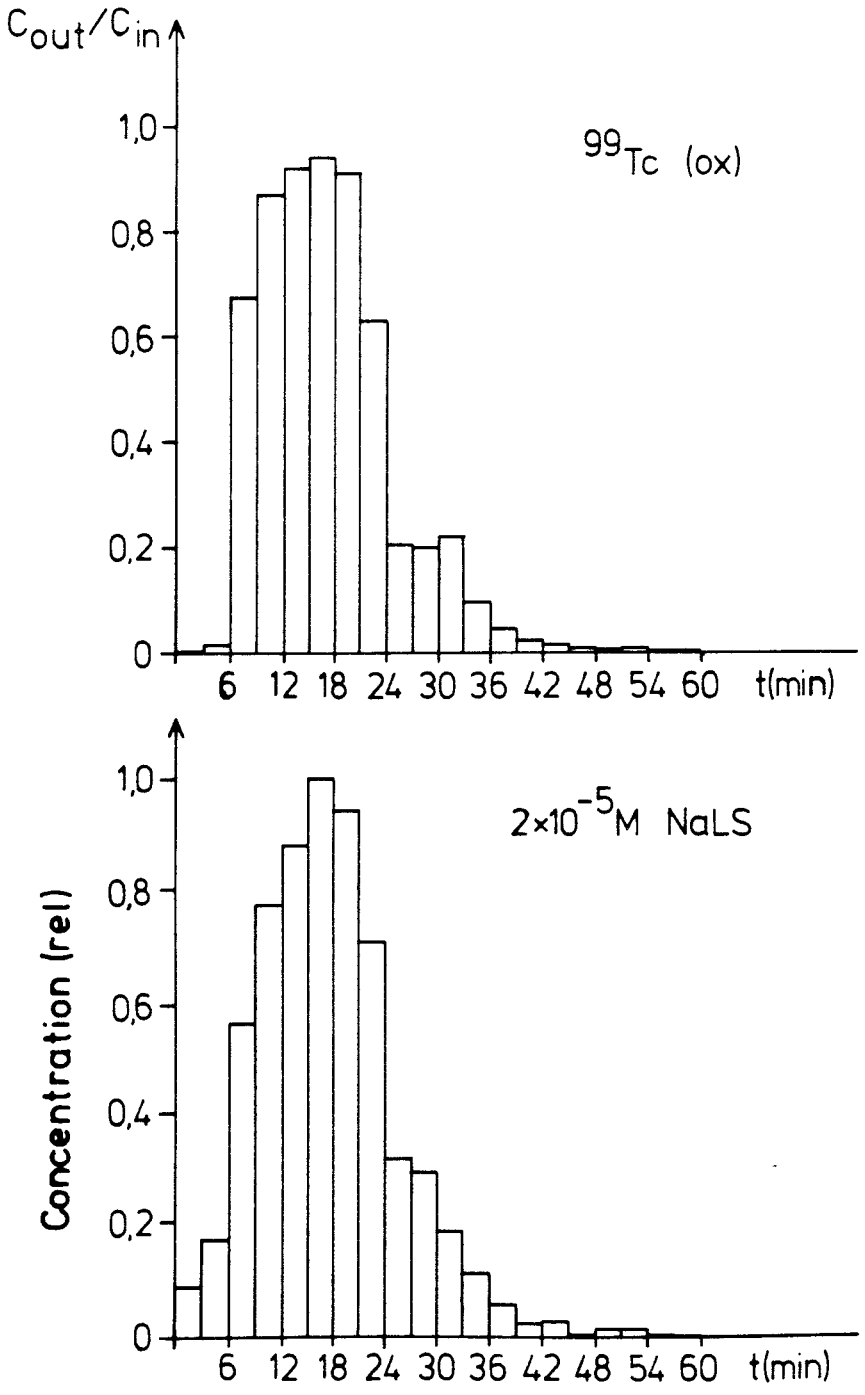


Figure 4.

Tracer concentration in eluate vs time.
Tracer pulse length 15 min.
Water flow 0.12 $cm^3 \cdot min^{-1}$.
Drill core Ø = 36 mm, 1= 80.

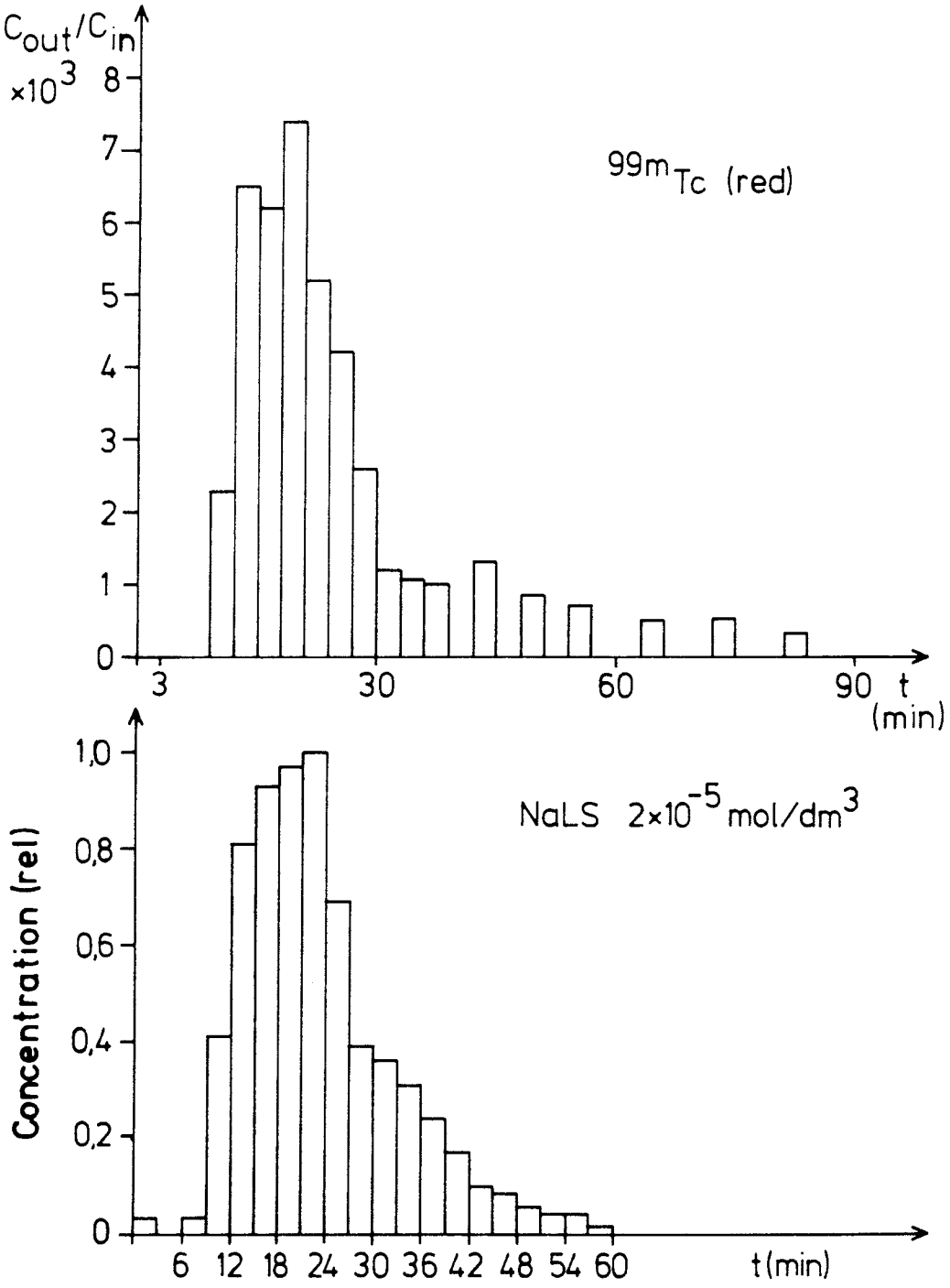


Figure 5.

Tracer concentration in eluate vs time.
Tracer pulse length 15 min.
Water flow 0.125 $cm^3 \cdot min^{-1}$.
Drill core Ø = 36 mm, l = 99 mm.

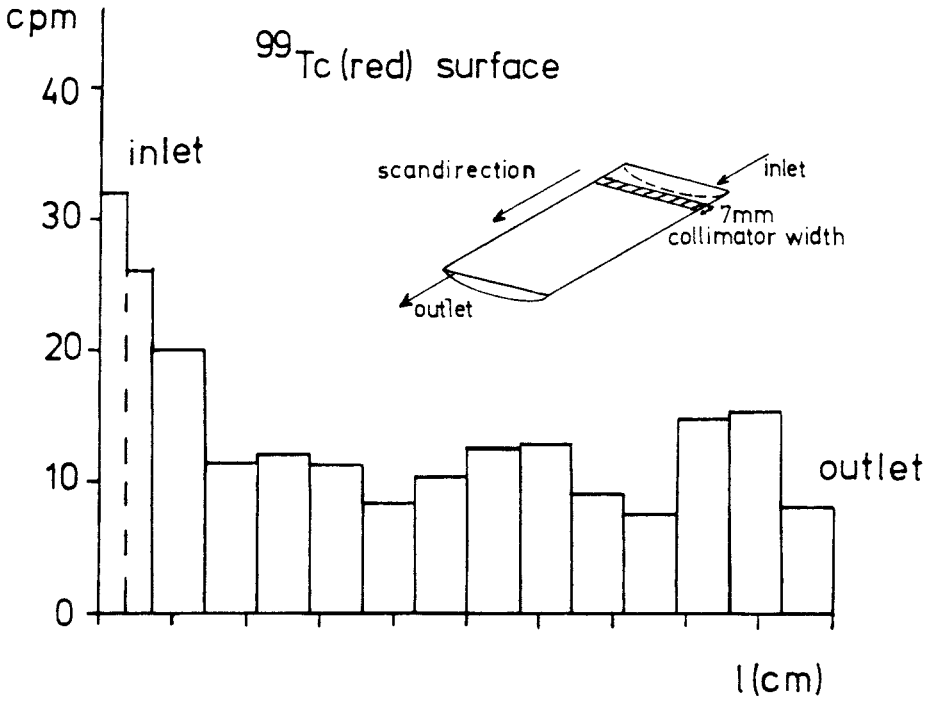


Figure 6.

^{99}Tc distribution as fissure surfaces 24 h after onset of tracer flow through fissure.
Ø = 36 mm, 1 = 99 mm, water flow 0.125 $cm^3 \cdot min^{-1}$ (flow data plotted in fig.4)

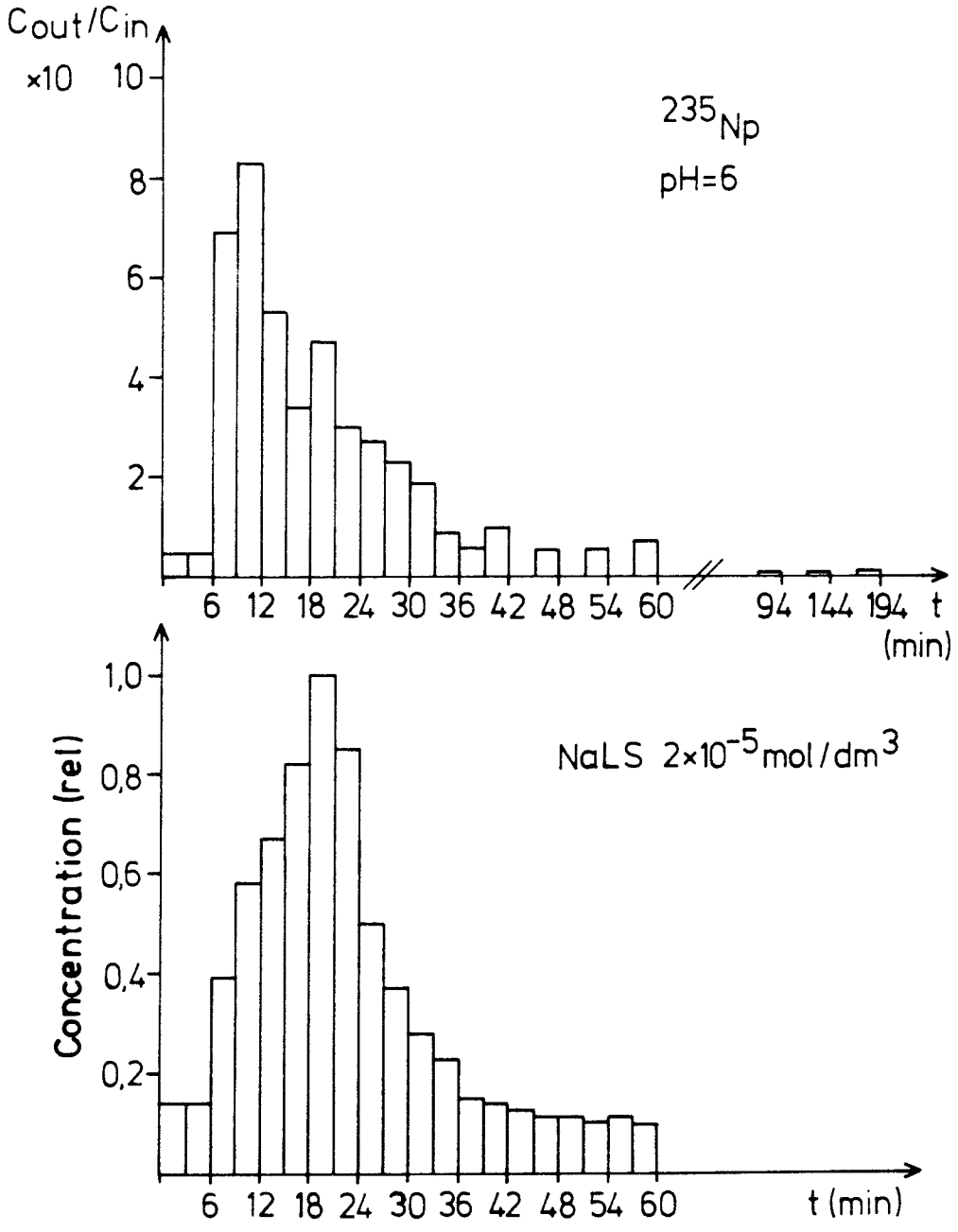


Figure 7.

Tracer concentration in eluate vs time.
Ø = 37 mm, 1 = 103.5 mm.
Water flow 0.12 $cm^3 \cdot min^{-1}$.
Tracer pulse length 15 min, eluation time 23 h.

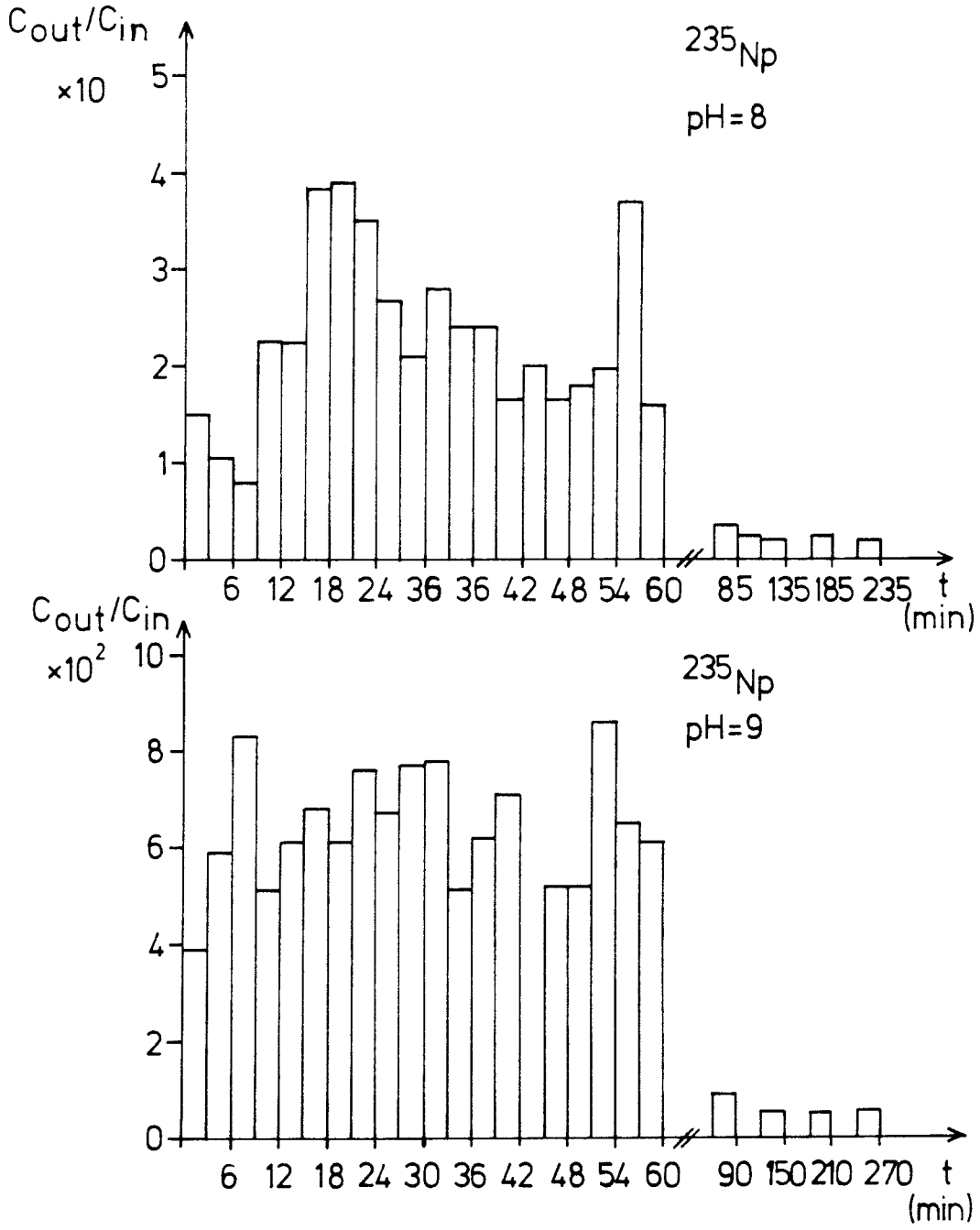


Figure 8.

Tracer concentration in eluate vs time
Ø = 37 mm, 1 = 103,5 mm.
Water flow 0.12 cm^3·min.
Tracer pulse length 15 min, eluation time 23.8 h.

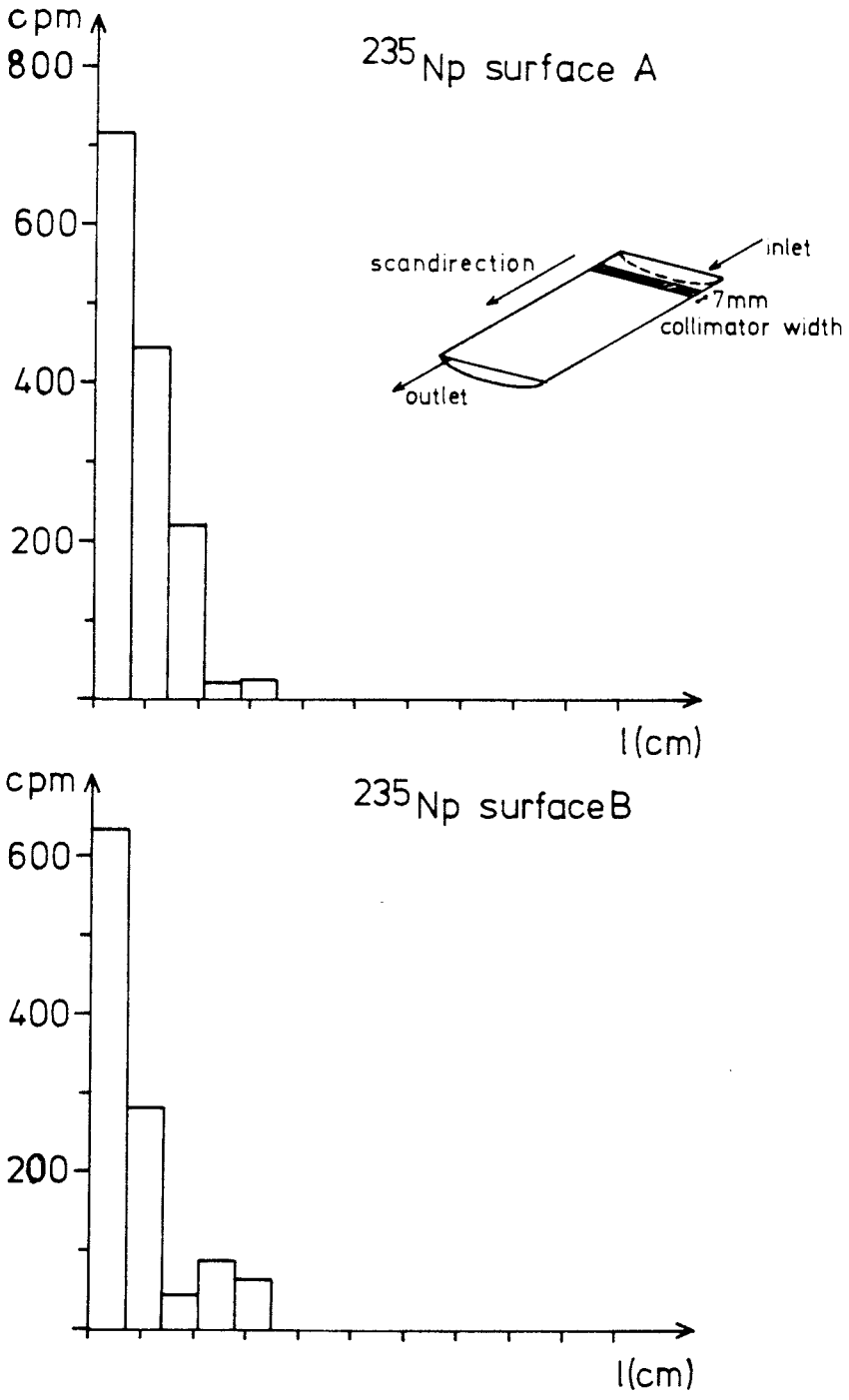


Figure 9.

Tracer distribution on fissure surfaces. 6.5 h after onset of tracer flow through fissure.
Ø = 37 mm, 1 = 104 mm, water flow 0.12 $cm^3 \cdot min^{-1}$, 15 min tracer pulse.

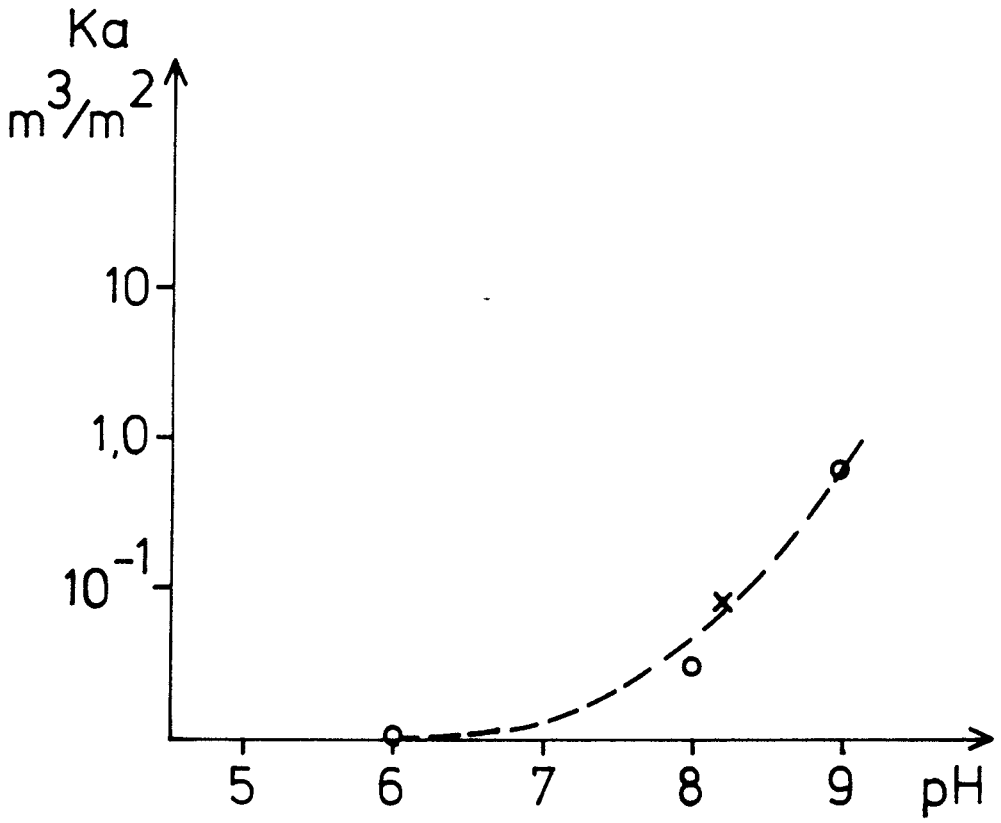


Figure 10.

^{235}Np: K_a values pH.

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1977–78
TR 121
KBS Technical Reports 1 – 120.
Summaries. Stockholm, May 1979.

1979
TR 79–28
The KBS Annual Report 1979.
KBS Technical Reports 79-01 – 79-27.
Summaries. Stockholm, March 1980.

1980
TR 80–26
The KBS Annual Report 1980.
KBS Technical Reports 80-01 – 80-25.
Summaries. Stockholm, March 1981.

1981
TR 81–17
The KBS Annual Report 1981.
KBS Technical Reports 81-01 – 81-16.
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1982
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The KBS Annual Report 1982.
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