Study of strontium and cesium migration in fractured crystalline rock

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IN FRACTURED CRYSTALLINE ROCK

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SUMMARY

The purpose of this investigation has been to study the retardation and dilution of non-active strontium and cesium relative to a non-sorbing substance (iodide) in a well-defined fracture zone in the Finnsjön field research area. The investigation was carried out in a previously tracer-tested fracture zone, see Gustafsson, Klockars (1981).

The study has encompassed two separate test runs with prolonged injection of strontium and iodide (run 1) and of cesium and iodide (run 2). The tests have shown that:

- Strontium is not retarded, but rather sorbed to about 40% at equilibrium.

- At injection stop, 36.3% of the injected mass of strontium has been sorbed and there is no desorption.

- Cesium is retarded a factor of 2-3 and sorbed to about 30% at equilibrium.

- At injection stop, 39.4% of the injected mass of cesium has been sorbed. Cesium is desorbed after injection stop (400 h) and after 1300 hours, only 22% of the injected mass of cesium is sorbed.

1. INTRODUCTION

Tracer tests and hydraulic tests have previously been carried
out in crystalline bedrock within the Finnsjön field research
area in order to characterize a fracture zone. Flow porosity
and dispersivity have been determined by using non-sorbing tra-
cers, see Gustafsson and Klockars (1981).

The purpose of the present investigation is to study the retar-
dation and dilution of non-active strontium and cesium relative
to a non-sorbing substance (iodide) in crystalline bedrock bet-
ween two boreholes in the well-defined fracture zone at the
Finnsjön field research area. The study has encompassed two
separate test runs with prolonged injection of strontium and
iodide in the first run and cesium and iodide in the second
run. The use of non-active strontium and cesium makes it neces-
sary to inject higher concentrations than in tests with
radioactive isotopes to obtain concentrations of tracer high
enough to separate from natural background concentrations.

Very few in situ migration experiments in fractured crytalline
rocks have so far been reported. Within the KBS project, tracer
tests in crystalline bedrock with non-sorbing substances have
previously been carried out at Studsvik (Landström et al 1978).
In these tests, the radioactive isotopes I-131 and Sr-85 were
used, among others. The tests were repeated at Studsvik within
an area with, in part, another rock type (Landström et al
1983). In these tests, the migration in two separate flow paths
was studied.

2. TEST AREA

2.1 General description

The Finnsjön field research area, situated east of Finnsjö Lake in
northern Uppland County (140 km north of Stockholm), comprises an
approximately 25 km^2 catchment area, see Fig. 2.1a. Annual
precipitation is about 685 mm (corrected) and evaporation is
estimated at about 475 mm. The topography is relatively flat, with
levels between 20 and 44 metres above sea level. The Quaternary
deposits, consisting mainly of moraine, are mostly of shallow
depth. The proportion of exposed rock is relatively high, nearly
20%. The bedrock is crystalline and consists of an older gneissic
granodiorite and young granite. Leptite occurs in the south and
north part of the area, along with deep greenstones in the north
part.

The geology, hydrology and groundwater conditions in the field
research area have been described by, among others, Almen et al
(1979), Olkiewicz et al (1979) and Scherman et al (1978).

2.2 Geology and topography

The test site is situated in the northwestern part of the Finnsjö
area adjacent to a crushed zone at Gåvastbo, see Fig. 2.2a. The
crushed zone runs in an approximate north-northwesterly direction,
its dip is steep and it appears in core borehole Fi 8 as a number
of parallel-displaced fracture zones.

Ten approx. 100 m deep percussion boreholes and two core boreholes,
460 and 730 m long, have been drilled within the test site. Fig.
2.2a shows the location of the boreholes and a schematic map of the
test site.

The test site can be described as a block of bedrock bounded in the
east by the crushed zone at Gåvastbo and in the north and south by
smaller, east-westerly marked fracture zones.

The outcropping block consists of a relatively well-exposed area, with for the most part deforested ground. Within the outcrop area, most of the fractures are steeply-dipping with a tendency to dip towards the east. The fracture rose diagram shows a fracture maximum at N50W, parallel to the foliation in the granite gneiss. The direction around N20W indicates a fracture minimum and coincides with the direction of the Gåvastbo line. A system of horizontal to southerly flat-dipping fractures is also observed in the outcrop.

The depression along the crushed zone east of the outcropping block is dominated by reforested cropland with small projecting outcrops. In the depression, the Quaternary deposits have a maximum depth of about 5 m. The rock is overlain by moraine, then clay and on top a thin layer of peat.

The rock mapped on the surface as well as in core borehole Fi 8 is a predominantly grey, medium-grained granodioritic-granitic gneiss granite. The composition of the rock type was determined from drillings from borehole G3 and is shown in table 2.2a (Skagius et al 1981).

Table 2.2a   Composition of the rock type

Mineral	Fraction
Quartz	39%
Plagioclase	26%
Microcline	17%
Biotite	6%
Hornblende	8%
Epidote	3%
Chlorite/calcite	1%

Occasional irregular veins of pegmatite and aplite traverse the gneiss granite, usually only up to 0.2 m wide. Quartz appears in isolated veins and, in places, as fracture filling. The most

common fracture coating minerals are calcite, prehnite, laumontite, chlorite and quartz.

2.3 Hydrogeology

The bedrock is relatively rich in water-bearing fracture and crushed zones in the upper 100 m, which is reflected in the ten percussion boreholes G1 - G10 within the area. The transmissivity obtained from short- and long-term test pumpings is, for the more capacitive boreholes in the depression, on the order of E-5 m^2/s. The hydraulic conductivity measured for 2 m sections of the boreholes by means of the water injection method indicates a wide scatter between individual measurement sections and between the different boreholes. Of the investigated borehole sections, hydraulic conductivity exceeds E-6 m/s in 5% of the number of measurement sections.

The natural groundwater flow within the test site should be expected to follow the topography generally, i.e. a flow from the outcropping block towards the depression at Gåvastbo. Water pressure measurements in existing boreholes indicate a downward-directed groundwater transport at the outcropping block, with an upward-directed flow of groundwater in the depression. Taken together, these observations give a picture of a three-dimensional groundwater flow with a recharge area comprising the outcropping block and a discharge area in the depression along the existing crushed zone. Along the depression and in the upper part of the crushed zone, a more or less horizontal groundwater flow with a northerly direction is judged to prevail.

The fracture zone between the injection hole G2, section 91-93 m and the pump hole G1, 100-102 m consists in borehole G2, according to TV logging, of 3-4 open fractures. The hydraulic conductivity of the fracture zone has been determined in tracer tests to be 2-3 E-3 m/s, Gustafsson, Klockars (1981). The flow in the fracture between the boreholes takes place in two main transport pathways with differing hydraulic properties, clearly distinguishable from the breakthrough curve. See Fig. 2.3a. Calculations of mean frac-

ture width for a fracture corresponding to the entire fracture zone
give a varying value depending on the calculation method. The mean
fracture width obtained from flow volume calculations is about 20
times greater (1.6 E-3 m) than that obtained from calculations
based on the relation of the hydraulic conductivity to the width of
a plane-parallel fracture. In the latter case, the narrower parts
of the fracture zone are determinant for the calculated fracture
width. In this case, the fracture width was calculated to be
7 E-5 m (0.07 mm). The kinematic porosity, calculated as the ratio
between the hydraulic conductivities of the rock mass and the
fracture zone, is 8-9 E-4.

2.4 Hydrochemistry

The water analyses carried out within the test area are summarized
in table 2.4a. The high chloride and sulphate contents indicate the
influence of relict seawater (Rennerfelt, 1977 and Jacks, 1978). In
general, the water has a high total salinity.

Groundwater that has infiltrated in forested areas is expected to
have low nitrate contents. The high nitrate contents and the wide
variation of the contents with time indicate contamination by
superficial groundwater. Water is pumped continuously from borehole
G1, with a drawdown of about 6-8 m below the top of the pipe. Water
leaks in from the Quaternary deposits at the 4 m level. The high
nitrate contents in the borehole probably derive from this leakage,
see table 2.4a.

Table 2.4a   Results of water analyses within the test area

		G1[1] 780413	G1[1] 780711	G1[1] 780830	G1[1] 781026	G1 6 m[1] 781111	G1[1] 800221	G1[1] 800229	G2 66 m 780227	G2 94 m 781030	G5 25 m 780704	G 10[1] 800221	G10[1] 800229	G1[1] 810706	G1[1] 810729
cond.	mS/m	190	255	205	230	210	280	280	190	135	135	216	211	325	307
pH		7.0	7.45	7.4	7.5	7.45	8.1	8.3	8.0	7.6	8.25	8.2	8.3	7.6	7.6
$KMnO_4$ elof	mg/l	27	21	20	32	24	30	31	27	25	15	26	24	21	20
tot hardness Ca	°	180	204	176	181	160	190	201	126	76	140	152	156	261	299
Ca	mg/l	152	168	148	146	132	161	161	99	61	105	126	133	218	251
Mg		17	22	17	21	17	21	21	16	9	21	15.5	13.5	26	29
Na		265	355	315	330	320	390	420	280	240	275	320	300	477	516
K		2.7	4.3	3.8	4.1	3.5	4.0	4.0	4.3	31	4.2	5.8	5.3	9.5	10
Cl	mg/l	577	720	620	635	600	716	724	445	330	600	540	524	830	950
SO_4		47	55	53	52	34	55	60	54	20	29	42	42	69	67
HCO_3		198	260	251	268	266	282	290	320	285	305	235	233	251	247
NH_4	mg/l	0.17	< 0.01	0.17	0.20	0.01	0.09	0.27	0.50	< 0.01	0.09	0.17	0.15	<0.01	0.27
NO_2		< 0.01	< 0.01	0.15	< 0.01	< 0.01	0.66	0.01	< 0.01	< 0.01	<0.01	0.06	0.0.	<0.005	0.023
NO_3		0.14	1.80	1.20	0.44	0.92	1.4	0.1	0.11	0.63	0.07	0.1	0.3	5.2	5
PO_4		< 0.01	< 0.01	< 0.01	< 0.01	0.01	0.01	0.02	< 0.01	0.02	0.01	0.03	0.01	<0.3	<0.03
tot Fe	mg/l	0.18	0.86	0.10	1.07	1.10	0.36	0.05	0.64	2.3	0.29	0.23	0.23	0.02	0.16
Fe elof								0.02	0.02				0.04	0.02	
Mn		0.30	0.24	0.24	0.18	0.22	0.26	0.27	0.22	0.11	0.06	0.16	0.16	0.35	0.38
F	mg/l	1.1	2.3	2.3	2.2	1.8	1.5	1.6	2.2	3.1	3.6	1.4	1.4	1.2	1.8
SiO_2		11.8	14	14	14	12	13	13	11.2	13	13	11	11	13.6	15
TOC		6.8	5.8	6.4	5.5	7.2	5.5	5.6	6.9	7.4	5.8	4.9	4.9		

Note[1] Pump water from all levels in the borehole

Loggings of pH, Eh and the conductivity of the borehole fluid in core boreholes Fi 6 and Fi 7 within the Finnsjön field research area (Duran & Magnusson, 1980) show Eh values between -60 and -120 mV at a depth of 50-100 m. Thus, reducing conditions prevail. Correlation was observed in the boreholes between increasing conductivity and decreasing Eh as well as between increasing pH and decreasing Eh.

The tracer tests were carried out in the local discharge area in the depression between boreholes G2, section 91-93 m and G1, section 100-102 m.

The water analyses from boreholes G1, G2, G5 and G10 in the valley, table 2.4a, show high conductivities and pH values. These boreholes are located in a discharge area. Reducing conditions are expected at depth in these boreholes.

The redox potential, Eh, does not affect the properties of strontium or cesium. On the other hand, changes in Eh can entail changes in the solid phase, i.e fracture-coating mineral and matrix, which can in turn affect the sorption of strontium and cesium.

Other parameters important for sorption of strontium and cesium are the groundwater's ionic strength, pH and "competing ions" - for strontium principally Ca^{2+} and for cesium K^+ and Na^+ (Lieser and Peschke, 1982). In addition, strontium can be sorbed through the formation of hydroxide, sulphate and carbonate complexes.

The groundwater within the area has a relatively high ionic strength. Ionic strength was calculated in three of the samples reported in table 2.4a (780711, 781026, 800229). The mean was 3.1 E-2 M.

The calcium and sodium concentrations in the groundwater pumped up from borehole G1 vary with time and are considerably higher than the values proposed for standard groundwater in KBS TR 36, TR 55 and in PRAV Report 4.29. In these reports, a calcium concentration of 18-50 ppm is proposed. At the time of the strontium test, the calcium concentration in the groundwater was 161 ppm. The sodium concentration has increased with time, and before the cesium test was started the concentration was about 500 ppm. The proposed concentration is 10-100 ppm. In most samples, the potassium concentration lies within the proposed range of 1.0-5.0 ppm. The sulphate concentrations are high compared to the values proposed in the above-cited reports, 47-67 ppm as compared to proposed 1.0-16.6 ppm.

The bicarbonate concentrations lie within the proposed range of 100-300 ppm. The water is supersaturated with respect to calcium carbonate. (At atmospheric pressure, equilibrium $CO_2(g) \overset{->}{\underset{<-}{}} CO_2(aq)$.)

Natural concentrations of strontium, cesium and potassium in the groundwater pumped out of borehole G1 are given in table 2.4b. The

mean strontium concentra on is 2.1 ppm, which is to be expected in
view of the high concent ation of calcium in the water, 146-251 ppm.
The ratio Sr/Ca is usually close to 0.01. In the groundwaters from
the Finnsjö area, Kråkemåla, Stripa and Studsvik with highly varying
groundwater types and calcium concentrations, the Sr/Ca ratio lies
within the range 0.007-0.012.

Table 2.4b   Summary of natural concentrations of strontium,
                cesium and potassium in the groundwater pumped out
                of borehole G1.

Date	Cesium (ppm)[1]	Potassium (ppm)	Strontium (ppm)
790110			1.7
790915			2.3
800717	-	-	2.3
800718	-	-	2.0
810623	< 0.1	4.6	
811014	< 0.1	5.1	
811104	"	3.1	
811203	"	2.6	
811230	"	5.1	
820122	"	5.1	
820215	"	4.6	
820312	"	5.4	
820326	"	3.3	
820401	"	3.6	
820507	"	-	
820527	"	-	
820523	"	-	
820921	"	-	

[1] Detection limit 0.1 ppm.

The cesium concentration is controlled primarily by water-mineral
reactions. In the water pumped out of borehole G1, the concentra-
tion is lower than 0.1 ppm (the detection limit of the analysis
method, AA). Previous to the present investigation the Cs con-
centration was 0.03 ppb, measured with neutron activation analysis.
In comparison, the cesium concentration is 0.02 ppb in the ground-
water pumped out from borehole B6N at Studsvik (Landström et al,
1983). In Stripa, the cesium concentration is 0.074 ppm in borehole
V-1, 764.7 - 856.7 m, and 0.046 ppm in borehole V-2, 763.7 - 877.7 m.

3. TRACER TESTS

3.1 Method and tracers used

In borehole G1, the groundwater table has been lowered by continuous pumping at constant capacity. In this manner, controlled groundwater conditions have been obtained within a given area with a groundwater flow directed towards borehole G1. The flow can be regarded as radially convergent, although the detailed flow is controlled by existing fracture pathways.

In borehole G2, section 91-93 m, tracer has been injected for subsequent detection in the water flow from pump hole G1. The distance between the injection zone and the fracture zone's outlet in the pump hole is about 30 m, see fig. 3.1a. Table 3.1a gives the pump flow and the head difference in metres of water between the injection hole G2 and the pump hole G1 on the test occasions.

Table 3.1a   Pump flow from G1 and head difference between
               injection hole G2 and pump hole G1.

Test	Pump flow (l/s)	Head difference G2 - G1 (m)
1	0.1	6.7
2	0.1	6.3

Injection of tracer solution is preceded by injection of groundwater from a nearby percussion borehole for a period of 2-3 days in order to adjust the flow, while a state of equilibrium is brought about in the groundwater head. The injection flow has been kept low in order to minimize disruption of the groundwater flow locally around the injection zone. Some variation in the injection flow has been unavoidable, which is reflected in some cases in the breakthrough curve.

Injection of tracers takes place over an extended period of time with continuous input to the fracture zone of a tracer solution prepared from tracers dissolved in groundwater to the desired concentration.

Injection flow, duration and total injected volume of tracer solution are shown in table 3.1b:

Table 3.1b   Mean injection flow, duration and total injected volume of tracer solution

Test	Mean injection flow	Duration	Injected volume
1	0.98 1/h	350 h	343 1
2	0.90 1/h	401 h	361 1

Tracers used, chemical form and concentration for the two test runs are presented in table 3.1c.

Table 3.1c   Tracers used, chemical form and injection concentration.

Test	Tracer	Chemical form	Concentration
1	I^-	NaI	6.67 E-2 M
	Sr^{2+}	$SrCl_2$	9.47 E-2 M
2	I^-	CsI	2.97 E-2 M
	Cs^+	"	2.97 E-2 M

The tracers were detected in the laboratory in samples of pumped-up water. An ion-selective electrode was used to detect iodide.

Strontium was detected with an emission spectrometer, IDES (Danielsson & Lindblom, 1976). Cesium was detected with an atomic absorption spectrometer.

3.2 Presentation of results

The results of the tracer tests are presented in the form of break-through curves, see Fig. 3.2a,b. Time after start of injection is given on the horizontal axis and recorded concentration in the pump flow at borehole G1 on the vertical axis, related to the injection concentration. The injection flow varied slightly with time; its mean value between observation occasions has been noted. An interruption in the injection of iodide/cesium occurred between 95 and 113 hours. The time of the interruption is somewhat uncertain, since it may have occurred gradually, but the start-up time is known. The recovery of tracers is presented in the form of recovery curves in fig. 3.2c-d. Time after the start of the injection is given on the horizontal axis and the accumulated quantity detected at the pump hole, related to the injected quantity, is given on the vertical axis.

4.   RETARDATION OF SORBING SUBSTANCES

4.1 General

In the present tests, the delay of sorbing substances is studied by comparing the transport of cesium and strontium with the transport of iodide. The results of previous studies show that iodide can be assumed to represent groundwater transport in the environment in which the tests have been carried out.

The tests show that cesium and strontium have a retardation and sorption relative to iodide that can depend on a number of chemical and physical processes, such as

1.   diffusion into the medium's matrix
2.   ion exchange
3.   adsorption
4.   reversible precipitation
5.   irreversible reactions with the medium
6.   complexing
7.   filtration effects

The additive effect of processes (2), (3), (4) and (5) is termed sorption. Sorption of a substance leads to a concentration decrease and a retardation of the migrating front relative to a non-sorbing substance. Complexings of a sorbing substance can lead to a more rapid material transport of the component. Filtration leads to a loss of the transported substance due to precipitations or colloidal effects.

Diffusion of the substance into the medium's matrix is determined by the effective pore diffusivity, which is the product of the pore diffusivity of the substance and the porosity of the matrix. Effective pore diffusivity is usually greater for sorbing substances than for non-sorbing ones.

Retardation can be expressed by means of a retention factor R, which is the ratio between the groundwater's mean retention time t_o

and the water-soluble sorbing substance's mean retention time t'_o according to

$$t'_o = R \times t_o \qquad (4.1.1)$$

The retention factor R includes the interaction of the substance dissolved in the groundwater with the solid phase (fracture-coating mineral/rock). If the retardation is a volume reaction, where sorption mainly takes place in the solid medium, R is written

$$R = 1 + K_d \, \rho \, \frac{1-\varepsilon}{\varepsilon} \qquad (4.1.2)$$

where K_d = volume adsorption coefficient

ρ = density of medium

ε = porosity of medium

If retardation in fractured bedrock is stuuied, where the entire rock mass is not available for reactions with the substance dissolved in the groundwater, the term $K_d \, \rho \, \dfrac{1-\varepsilon}{\varepsilon}$ is multiplied

by a factor representing the portion of the rock mass exposed to the groundwater and available for sorption reactions. (Torstenfelt et al 1981).

If sorption takes place mainly on the surface, the retention factor R is written

$$R = 1 + a \times K_a \qquad (4.1.3)$$

where a = active surface area per unit volume of solution

K_a = surface adsorption coefficient for the substance

In the event the transport is studied in a plane-parallel fracture with no roughness and a fracture width e, a can be written

$$a = \frac{2}{e} \qquad (4.1.4)$$

4.2 Interpretation

Interpretation of retardation in tracer tests in situ is based as a rule on laboratory determinations of the distribution coefficient K_d, which is a static measure of the sorption capacity of a solid material for a substance in solution, defined by

$$K_d = \frac{q_A}{C_A} \qquad (m^3/kg) \qquad (4.2.1)$$

where q_A = sorbed quantity of substance A on the solid phase at equilibrium (mol/kg)

C_A = concentration of substance A in solution at equilibrium (mol/m^3)

Studies of sorption or retardation are normally carried out in the laboratory by means of batch or column tests. In batch tests, the distribution coefficient can be calculated with the assumption of a state of equilibrium from the relationship

$$K_d = \frac{Vaq}{m} \times \frac{C_A{'}o-C_A}{C_A} \qquad (4.2.2)$$

where Vaq = solution volume (m^3)

m = mass of the solid phase (kg)

$C_A{'}o$ = original concentration in solution (mol/kg)

C_A = concentration in solution at equilibrium

In column tests, the retardation of a sorbing substance relative to that of a non-sorbing substance is determined in connection with flow through a column of fractionated material. K_d is then calculated from the relationship in eq. (4.1.2).

If sorption is primarily a surface reaction, a surface-based distribution coefficient, K_a, can be written as follows:

$$K_a = K_d \times \frac{\rho}{a_v} \qquad (m^3/m^2) \qquad (4.2.3)$$

where a_v = specific area (m^2/m^3 of solid material)

The results of determinations of distribution coefficients from batch tests and column tests can be dependent on the contact time and on physical and chemical parameters and are consequently not unambiguous.

Tests of the sorption of cesium and strontium have been carried out for KBS at KTH (the Royal Institute of Technology in Stockholm), CTH (the Chalmers University of Technology in Gothenburg) and Studsvik Energiteknik AB. Laboratory-determined K_d values are given in table 4.2.a for Sr and Cs, measured on Finnsjö granite and on the most commonly occurring fracture-coating minerals in the area.

Table 4.2a   Distribution coefficients, K_d, for Sr and Cs in synthetic groundwater, pH 8-8.5. Tracer concentration $\cong$ E-8 M (Landström et al 1983).

Rock type/mineral	K_d (Sr) (m^3/kg)	K_d (Cs) (m^3/kg)
Finnsjö granite	0.020	0.490
Calcite	0.001-0.003, 0.004[a]	0.001, 0.006[a]
Prehnite	0.010, 0.016[b]	0.013, 0.048[b]
Laumontite	0.029	0.117
Chlorite	0.050	0.129
Quartz	0.001-0.002	0.001
Pyrite	0.003	0.003

a)   Fracture face from Finnsjön

b)   Fracture face from Finnsjön, containing 10% calcite

Torstenfelt et al (1981) give the following values of K_d for Sr and Cs measured on crushed Finnsjö rock and calcite, see table 4.2.b.

Table 4.2b K_d values from batch tests on particle fractions
              0.09-0.25 mm

Rock type/ mineral	pH	Contact time	Kd (m^3/kg)	
			Sr(10 E-7 M)	Cs (10 E-7 M)
Finnsjö	7-9	1 day	0.015	0.262
gramote		1 week	0.014	0.331
		3 months	0.012	0.473
		6 months	0.018	0.664
Calcite	8-9	1 day	0.001	0.001
		1 week	0.002	0.002
		3 months	0.001	0.003
		6 months		0.003

The table shows that the K_d value does not change appreciably with
time. This applies in particular to Sr, which indicates a rapid
surface reaction. For Cs, an increased K_d value is observed with
time, which is assumed to be caused by a more volume-dependent
reaction.

Skagius et al (1981) have studied the time dependence of the
adsorption/desorption of Sr and Cs on crushed rock material of
different fractions. The purpose was to determine adsorption
capacity and diffusivity on crushed rock material from Finnsjön
and Stripa. Equilibrium between solid phase and solution is reach-
ed after 100 to 10 000 hours, at which point the adsorption tests
were interrupted and the desorption tests started. Evaluation of
the test has revealed that the sorption equilibrium for Sr is near-
ly linear at concentrations up to about 10 ppm, i.e. independent
of concentration in the solution, while the equilibrium is for Cs
non-linear. At equilibrium, the relationship between the quantity
sorbed by the medium and the concentration of the substance in
solution has been described with a Freundlich isotherm:

$$q = k \times C_p\beta \qquad\qquad (4.2.4)$$

where q   = concentration on the solid material

C_p = concentration in solution

k,β = constants

If the equilibrium relationship is linear, i.e. $\beta = 1$, the constant $k = K_d$, i.e. the distribution coefficient acccrding to the definition (eq. 4.2.1).

The experimental results indicated that the particles acted as porous bodies where two sorption processes were considered to exist: a rapid reversible surface sorption and a slow reversible set up, representing volume adsorption, k_v, and surface adsorption, k_A, see table 4.2c.

Table 4.2c   Parameter determination of Freundlich isotherms according to Skagius et al (1981)

	Finnsjön		Stripa	
	Sr	Cs	Sr	Cs
β	0.93	0.54	1.07	0.66
k_V	0.79 E-2	3.0 E-2	0.13 E-2	0.39 E-2
k_A	0.7 E-4	1.9 E-4	0.66 E-4	1.2 E-4

The table shows that obtained sorption capacity is greater for Cs than for Sr in Finnsjö rock. Observe that the equilibrium constant for Cs is not linear, i.e. that the sorption is concentration-dependent. This makes it difficult to utilize laboratory values in field measurements under dynamic conditions.

5.   TEST RESULTS AND INTERPRETATIONS

5.1 Dilution and dispersion

The concentration of tracer in a fracture during transport from the
injection hole to the pump hole is - for a non-sorbing substance,
at continuous injection, radial flow and steady state - equal to
the injection concentration. The hydrodynamic dispersion (longi-
tudinal component) and the macrodispersion - see Gustafsson,
Klockars (1981) - do not influence the concentration when the
breakthrough curve levels out. The transverse component of the
dispersion and the molecular diffusion lead to some dilution of the
substance in the fracture, but this is generally considered
neglible, especially with radially convergent flow. The reason why
the tracer concentration in the pump flow at borehole G1 (figs.
3.2a, 3.2b) is lower than the injection concentration, C_0, is
because the flow of tracer solution from borehole G2 comprises only
a limited portion of the total flow from the fracture zone to pump
hole G1. Further dilution of the tracer also occurs in the pump
hole with water from other fracture zones, see figs. 3.1a and 3.1b.
Thus, at equilibrium, the concentration of tracer in the pump flow
at G1 will be determined by the ratio of injection-flow/pump-flow.

If the diffusion and transverse dispersion of the iodide is neglible,
the volume of the fracture system through which the tracer solution
is transported between boreholes G2 and G1 is equal to the difference
between injected and recovered volume of tracer solution. When the
breakthrough curve for iodide in tests 1 and 2 has levelled out,
the difference between injected and recovered volume at an arbitrary
point in time is 5.1 E-2 m^3. With compensation for the volume
between the packers in the injection hole G2 (0.7 E-2 m^3), the
volume of the fracture system through which the tracer solution is
transported is 4.7 E-2 m^3.

The flow between boreholes G2 and G1 takes place in two main trans-
port pathways, clearly distinguishable from the breakthrough curve,
see fig. 2.3a. The volume of the primary transport pathway, calculat-

ed in the same manner as the volume of the entire fracture system, is 3.3 E-2 m^3.

During tests 1 and 2, the injection flow between the packers in borehole G2 was twice the natural flow through the borehole at the given gradient. The extent of the injection zone in the horizontal direction at borehole G2 can thereby be approximated to four bore-hole diameters, i.e. 0.44 m in tests 1 and 2.

In radially symmetric flow model with a horizontal extent of 0.44 m at a radius of 30 m and the volumes given above, the mean fracture width is 5.0 E-3 m for the primary transport pathway and 2.1 E-3 m for the secondary transport pathways.

5.2 Sorption and retardation

In in situ tests with sorbing (reactive) substances, a complex interaction exists between different chemical and physical processes between the substance dissolved in the groundwater and the sorbing solid material.

Of special importance for the sorption of Sr and Cs are:

- the concentration of the substance
- the composition of the groundwater (ion strength, "competing" substances, complexing agents, pH)
- the composition of fracture mineral/rock type (ion exchange capacity, active surface, porosity)

Flow geometry and injection concentration have given a concentration of sorbing substances in the fracture that far exceeds the concentration used in laboratory tests for K_d and K_a determinations. K_d is concentration-dependent, which is why calculations of retardation and sorption for the field tests using laboratory-determined K_d values are not fully reliable.

The groundwater's composition deviates from the standard water of "Allard type" used in laboratory tests, see section 2.4.

Ionic strength is 3-4 times higher in the Finnsjö groundwater than in the synthetic groundwater prepared in the laboratory. An increase of ionic strength reduces sorption capacity, Anderson et al (1982).

The main competing ions are Ca and K ions, where the Ca concentrations in some cases are more than a power of 10 higher in the Finnsjö groundwater than in the standard water. According to Bauchhuber et al (1982), the sorption of Sr is reduced considerably by the addition of Ca and K ions. A similar relationship exists for Cs sorption with the addition of K and Ca ions, but the sensitivity to Ca ions is less.

High concentrations of HCO_3 and SO_4 in the groundwater, see section 2.4, may lead to precipitations of Sr. The possible amount of Sr sorbed by precipitation of $SrCO_3(s)$ and $SrSO_4(s)$ was computed with the equilibrium model SOLGASWATER. In the tracer solution, prepared from tracers dissolved in groundwater, 3% of the total amount of Sr precipitates, of which 78% precipitates as $SrCO_3(s)$ and 22% as $SrSO_4(s)$. In the fracture zone between boreholes G2 and G1, additional amounts of Sr will precipitate as $SrCO_3(s)$ and $SrSO_4(s)$. At continuous injection to the fracture zone and prevailing flow geometry and groundwater chemistry, the precipitation of Sr was computed at different extents of mixing between tracer solution and fracture groundwater. With improbable heavy mixing 3% will precipitate, i.e. a total of 6% Sr will be lost by precipitation.

The Finnsjö groundwater (and other natural groundwaters) deviates from standard water also in that it contains natural background concentrations of the sorbing substances being studied. The background concentration of Sr is about 2 ppm, while the concentration of cesium lies below the measuring limit <0.1 ppm. Water analysis, with neutron activation analysis, performed previous to the present investigation shows that the cesium concentration is about 0.03 ppb.

The present field tests were carried out in a fracture zone at a depth of about 100 m. The pump hole was chosen so that the imposed flow direction coincides closely with the natural one. Equilibrium

between fracture-coating minerals and recent groundwater is assumed
to exist. The most commonly occurring fracture-coating mineral in
the area is calcite (Tullborg, Larsson 1983). This, together with
the prevailing chemical environment, leads to the assumption that
the substances dissolved and transported in the groundwater are
primarily in contact with calcite in the fractures.

The breakthrough and recovery curves, figs. 3.2a-3.2d, show that Sr
and Cs are retarded and sorbed relative to iodide. The retardation
of Sr is, however, minimal.

The retardation of Sr and Cs relative to the reference tracer
iodide has been calculated from the breakthrough curves as the
ratio between the times for 5% breakthrough, t'(5%)/t(5%), and
between the times when the breakthrough curves level out,
t'(∞)/t(∞). Calculated retardation is given in table 5.2a in
the form of the retention factor.

Table 5.2a   Calculated retention factor, R, for Sr and Cs
              relative to iodide.

Tracer combination	t'(5%)/t(5%)	t'(∞)/t(∞)	t'/τ(mean)
Sr/I	1.2	1.1	1.15
Cs/I	2.8	2.2	2.50

On the basis of the obtained retention factor, R, and with calcite
as the sorbing mineral, the factor, f, representing the fraction of
the rock mass exposed to groundwater flow and available for
sorption reactions is calculated as follows:

$$R = 1 + K_d \, \rho \, \frac{1-\varepsilon}{\varepsilon} \times f \qquad (5.2.1)$$

The flow porosity, Θ_k (kinematic porosity), is an expression for the fraction of the rock mass in which the groundwater flow takes place. The flow porosity has previously been determined for the fracture zone between boreholes G2 and G1 (Gustafsson and Klockars 1981). The flow porosity Θ_k, and the factor f are given in table 5.2b.

Table 5.2b   Flow porosity, Θ_k, and factor f calculated
with calcite as the sorbing mineral

Tracer	R	Kd (m^3/kg)	ρ (kg/m^3)	ε	f	Θk
Sr	1.15	0.004	2 700	0.005	7.0 E-5	8.5 E-4
Cs⁻	2.50	0.006	"	"	4.6 E-4	8.5 E-4

Calculations are sensitive to the values chosen for input parameters. Uncertainty in this calculation is great in particular with regard to the representativeness of the distribution coefficient, K_d, at high concentrations. Cs has a non-linear sorption isotherm. The same applies to Sr above 10-20 ppm, i.e. in the present tests. Porosity is also of great importance.

When the breakthrough curves level out, the concentration of Cs is 0.71 times the iodide concentration, and that of Sr 0.59 times the iodide concentration. This would mean that Cs is sorbed to a degree of 29% and Sr to 41%. The sorption of Sr is, however, lower than the sorption of Cs in the initial phase.

Sorption relative to iodide, calculated as the difference in recovery between iodide and sorbing substance, is given in figures 5.2a and 5.2b. Cesium shows a relatively rapid sorption, which turns into desorption after half the injection time.

At injection stop, 36.3% of the injected mass of strontium has been sorbed, which is equivalent to 11.8 moles of Sr (1033 g Sr). After injection stop, no desorption of Sr takes place.

At injection stop, 39.4% of the injected mass of cesium has been sorbed, which is equivalent to 4.2 moles of Cs (561 g Cs). Desorption continues after injection stop (400 h) and after 1300 hours only 22.0% of the injected mass of Cs is sorbed (2.4 moles, 313 g Cs).

6.   DISCUSSION AND CONCLUSIONS

Field tests carried out with the sorbing substances strontium and cesium, with iodide as a non-sorbing reference tracer, have given the following results:

-    Strontium is not retarded, but rather sorbed tc about 40% at equilibrium.

-    Cesium is retarded by a factor of 2-3 and sorbed to about 30% at equilibrium.

The amount of Sr lost by precipitation was computed with the equilibrium model SOLGASAWATER: Only 6% is lost by precipitation. Thus, most, about 35%, is lost by other sorption mechanisms.

Retardation and sorbtion were minimal compared to expected values, based on laboratory-measured K_d values on crushed rock material.

One hypothesis for interpreting the experimental results is that the fracture walls are coated with calcite of a given thickness. Calcite is the most frequent fracture-coating mineral in the test area and the most probable, in view of the chemical environment prevailing today. The ratio between measured K_d values for calcite and crushed Finnsjö rock is about 1:10 for strontium and about 1:200 for cesium. This would explain in part the low retardation of these substances.

The difference in recovery of sorbing substances relative to iodide is explained by an inward transport, caused by the concentration gradients of the respective substances, through the fracture-coating mineral and into the microstructure of the rock. The rock type has high sorption capacity, so that once the substance has diffused through the fracture-coating mineral, it is "sucked up" and is no longer readily accessible for exchange processes.

The transport rate of strontium, which coincides closely to that of the non-sorbing substance, is explained by the fact that available

sites for surface sorbtion are already occupied by naturally
occuring strontium and high concentrations of competing ions.
This interpretation agrees well with the low desorption of
strontium after the injection has been concluded.

The retardation of cesium is explained in a similar manner by
an active surface sorption which is saturated in time by a
surplus of cesium, and equilibrium is established in the surfa-
ce sorption. The breakthrough curve levels out and the volume
sorption becomes the crucial sink. The surface sorption is
reversible, which is shown at injection stop between 93 and 113
hours, when cesium is desorbed and the concentration in the
pump water does not decline as sharply as that of the non-sor-
bing substance. After the injection has been concluded, cesium
is desorbed to a higher degree than strontium.

The concentrations of Sr and Cs in the fracture zone exceed the
concentrations used in laboratory test for K_d and K_a deter-
minations. In the case of Cs, K_d is concentration-dependent.
The same applies to Sr above 10-20 ppm, i.e. in the present
test. That is why calculations of retardation and sorption for
the field tests using laboratory-determined K_d values are not
fully reliable. This may in some part explain the great diffe-
rence between obtained and predicted retardation and sorption.
However, it should be noted that previously performed tracer
tests in crystalline bedrock at Studsvik (Landström et al 1978,
1983) with low concentrations of Sr-85 showed lower retardation
than corresponding laboratory column tests on crushed Studsvik
rock.

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        and Stuasvik Sweden. Identification, chemistry and
        dating. KES Technical Report 82-20.

LIST OF FIGURES

Fig. 2.1a   Map showing location of Finnsjö field research
            area
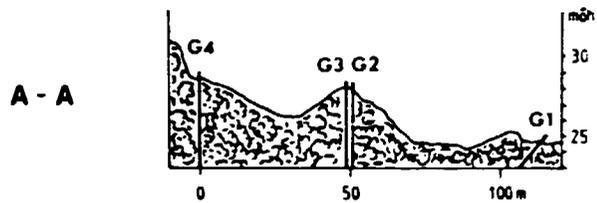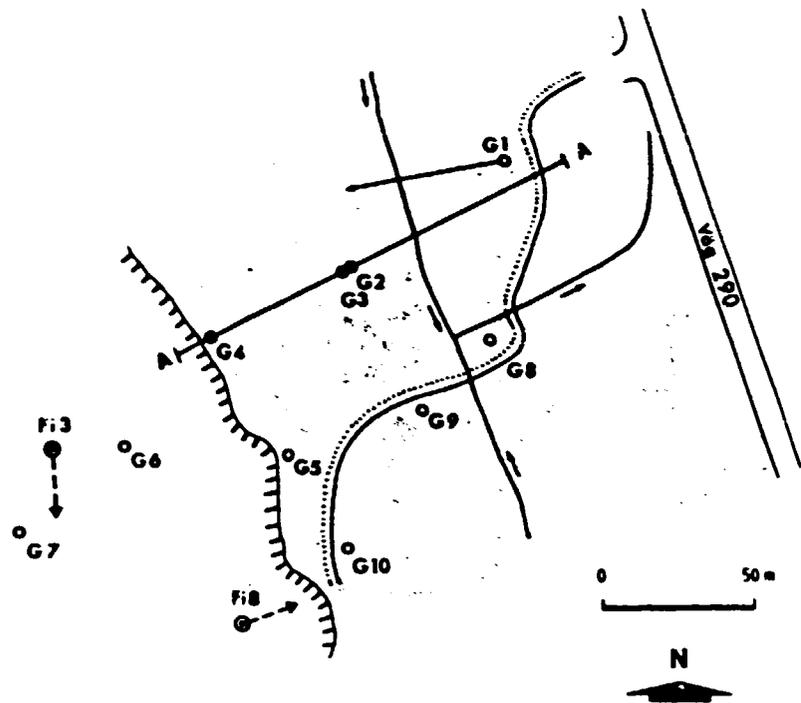
Fig. 2.2a Schematic map of test site showing location of
boreholes
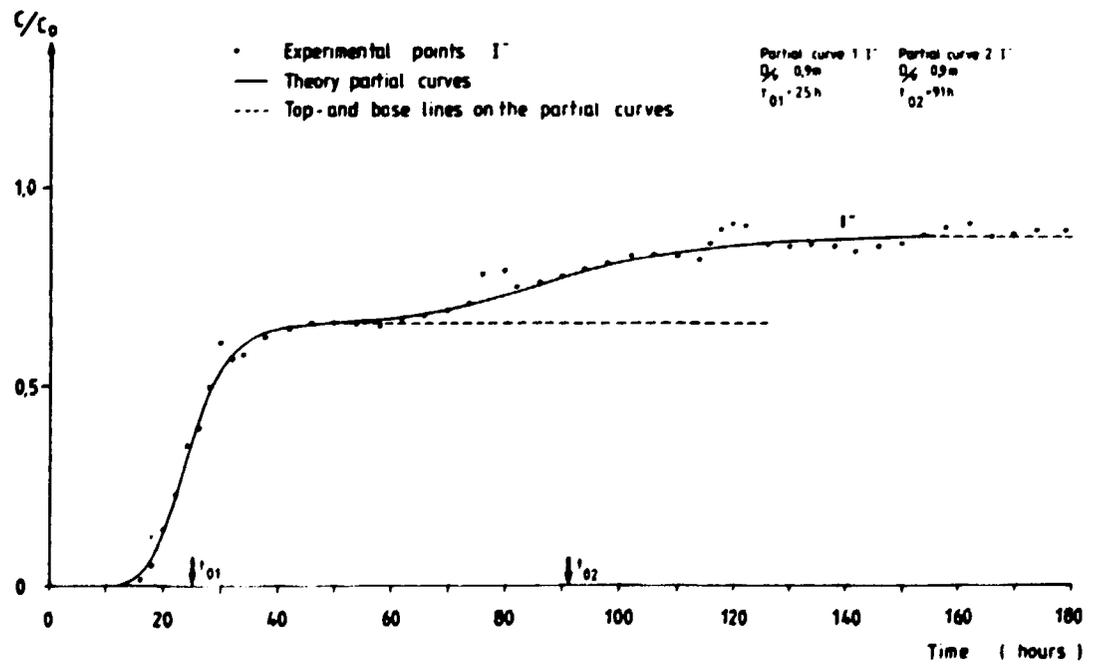
Fig. 2.3a Experimental breakthrough curve for I^- in run 1
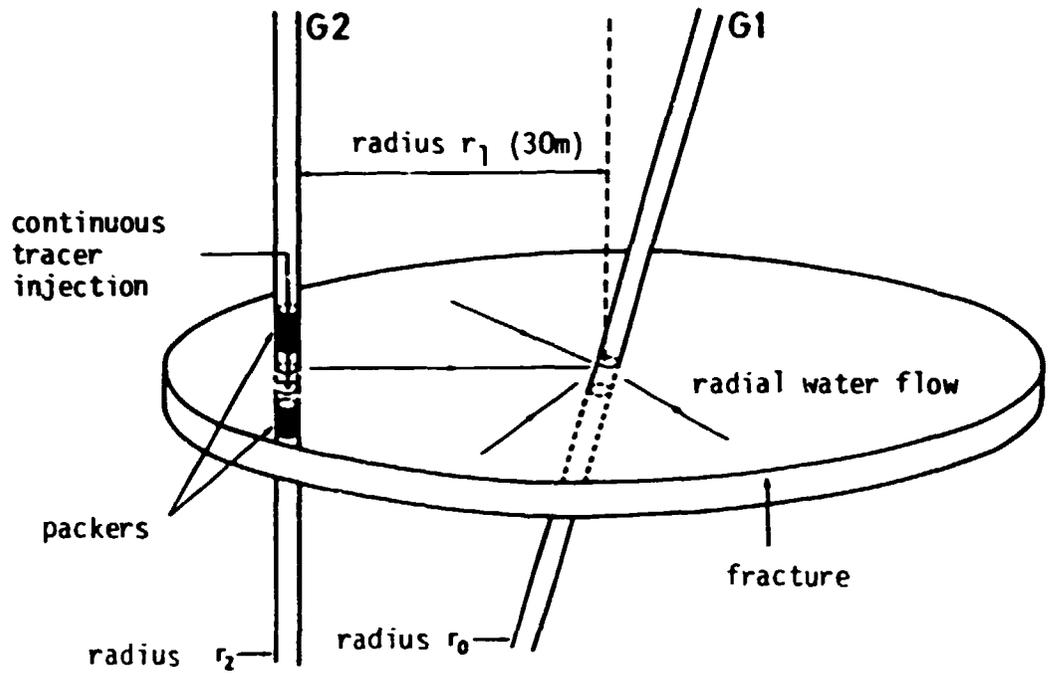and fit with two theoretical curves
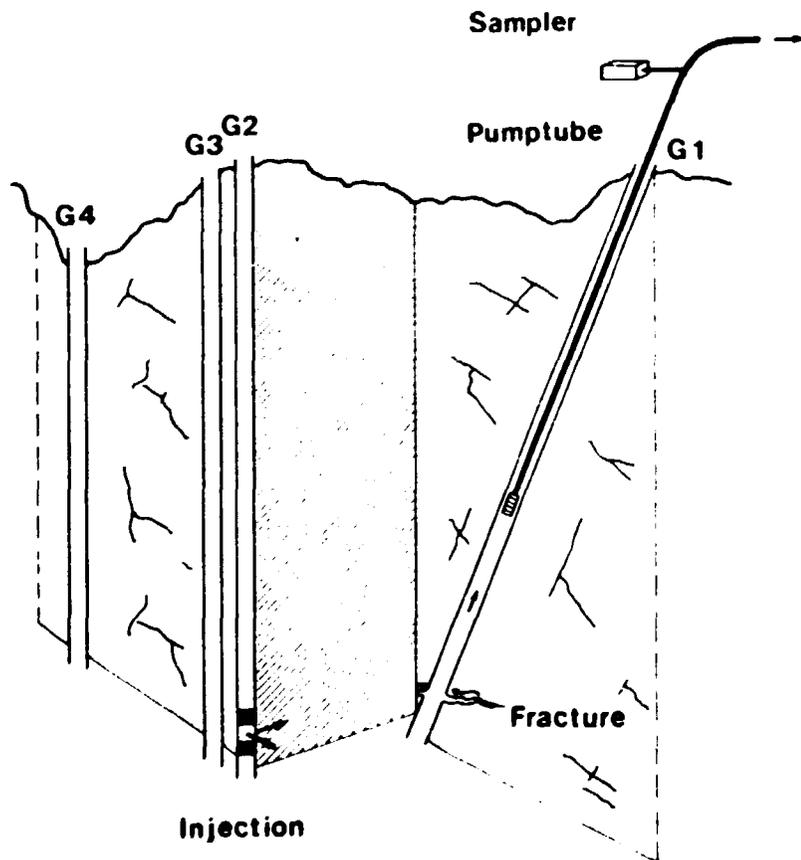
Fig. 3.1a Radial water flow model

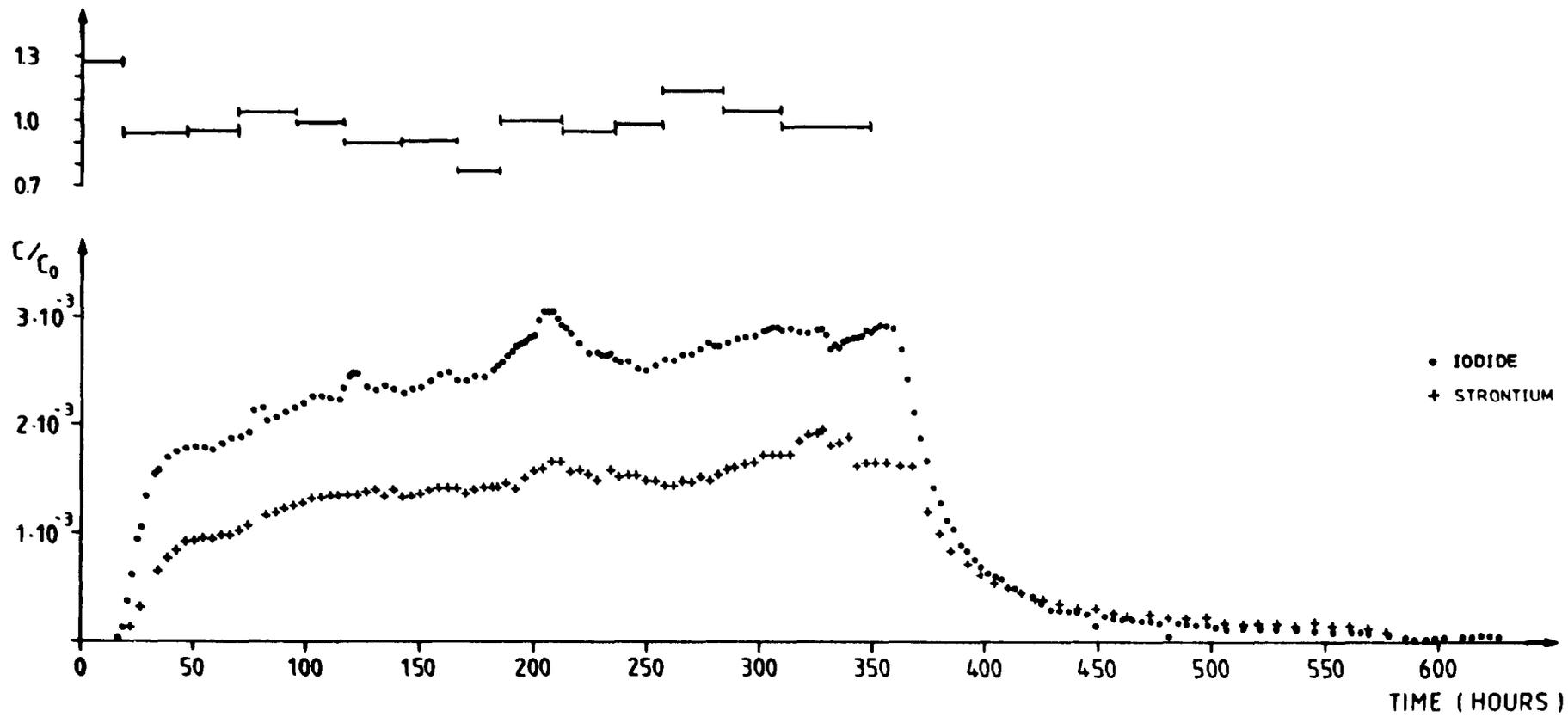Fig. 3.1b Cutaway view of test site and instrument set-up

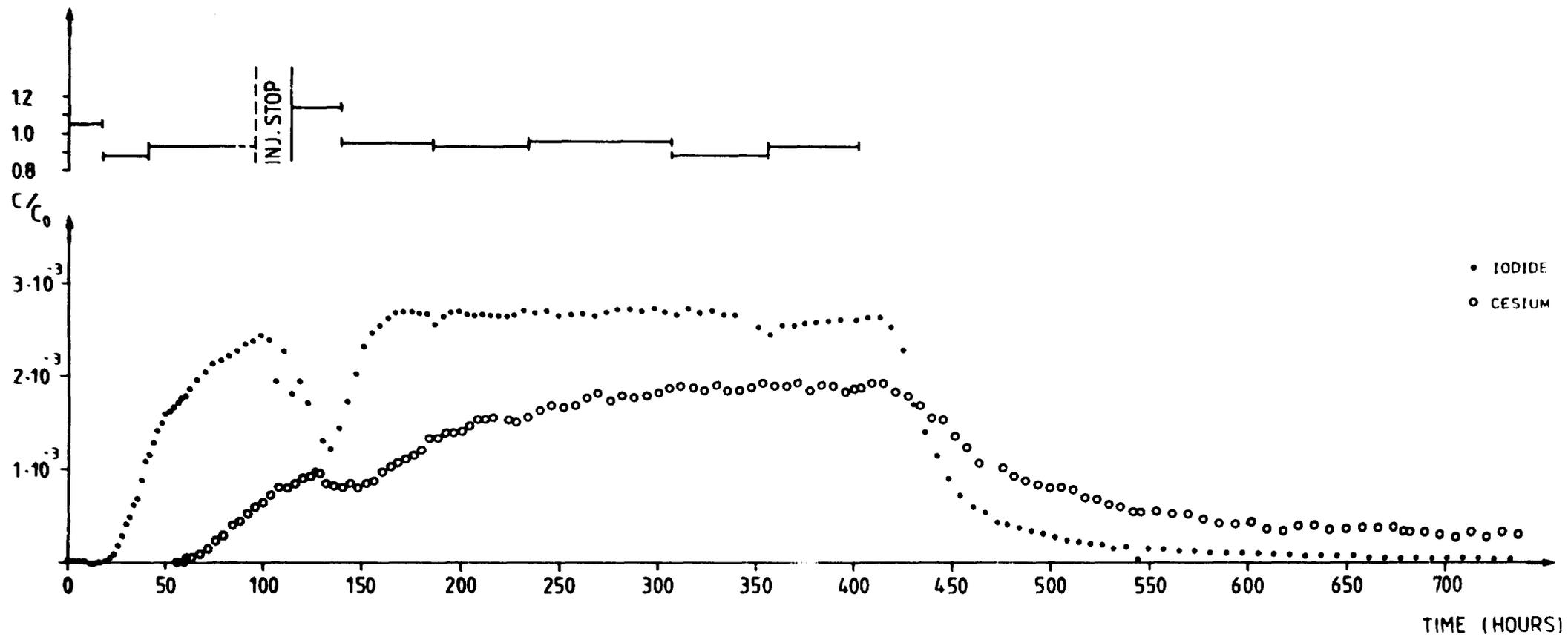Fig. 3.2a   Breakthrough curves for iodide and strontium in
            run 1

Fig. 3.2b   Breakthrough curves for iodide and cesium in
             run 2
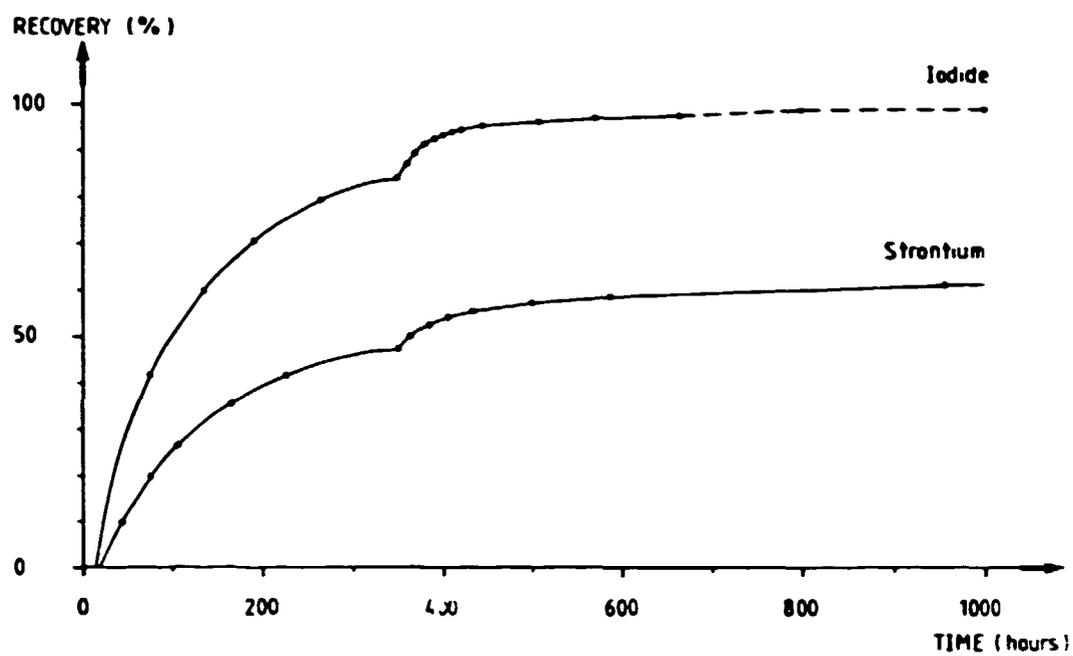
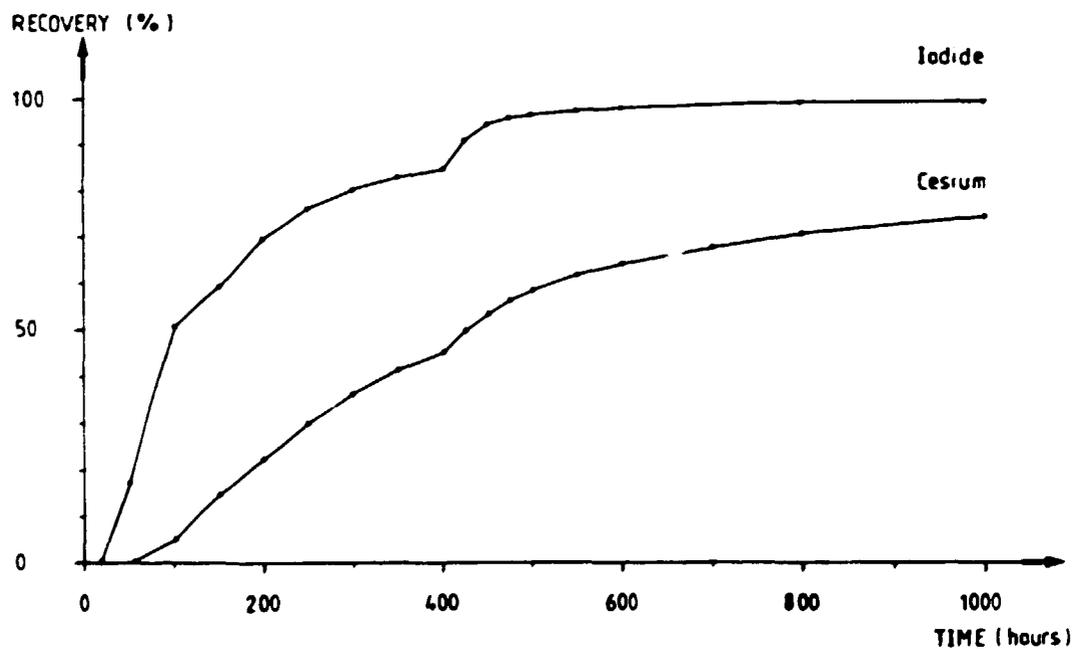Fig. 3.2c Iodide and strontium recovery relative to accumulated injected mass

Fig. 3.2d Iodide and cesium recovery relative to accumulated injected mass
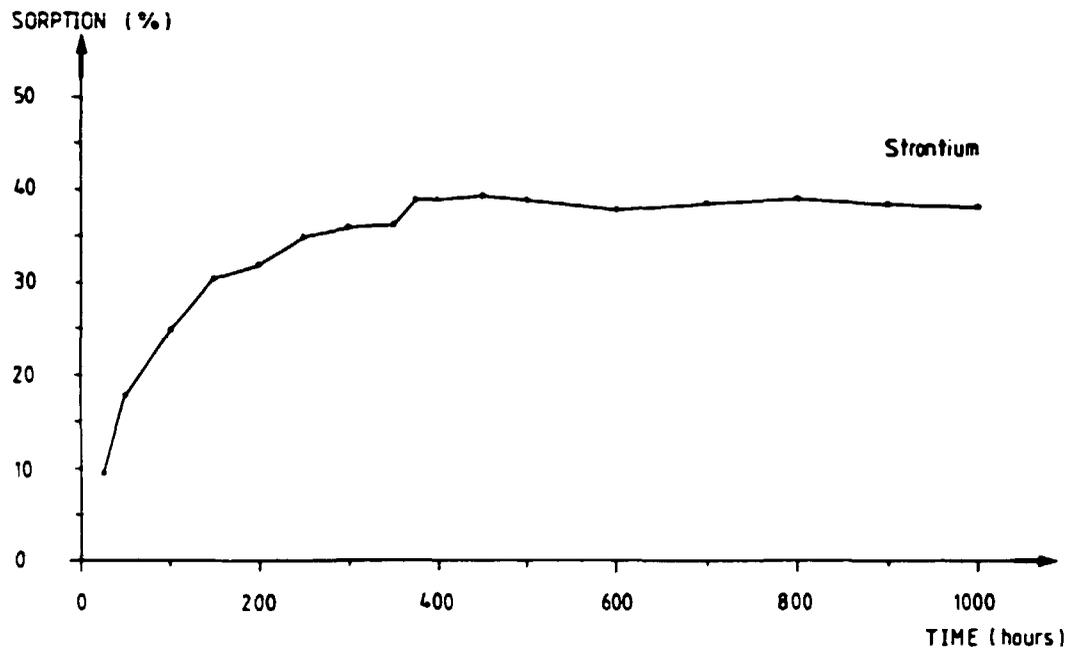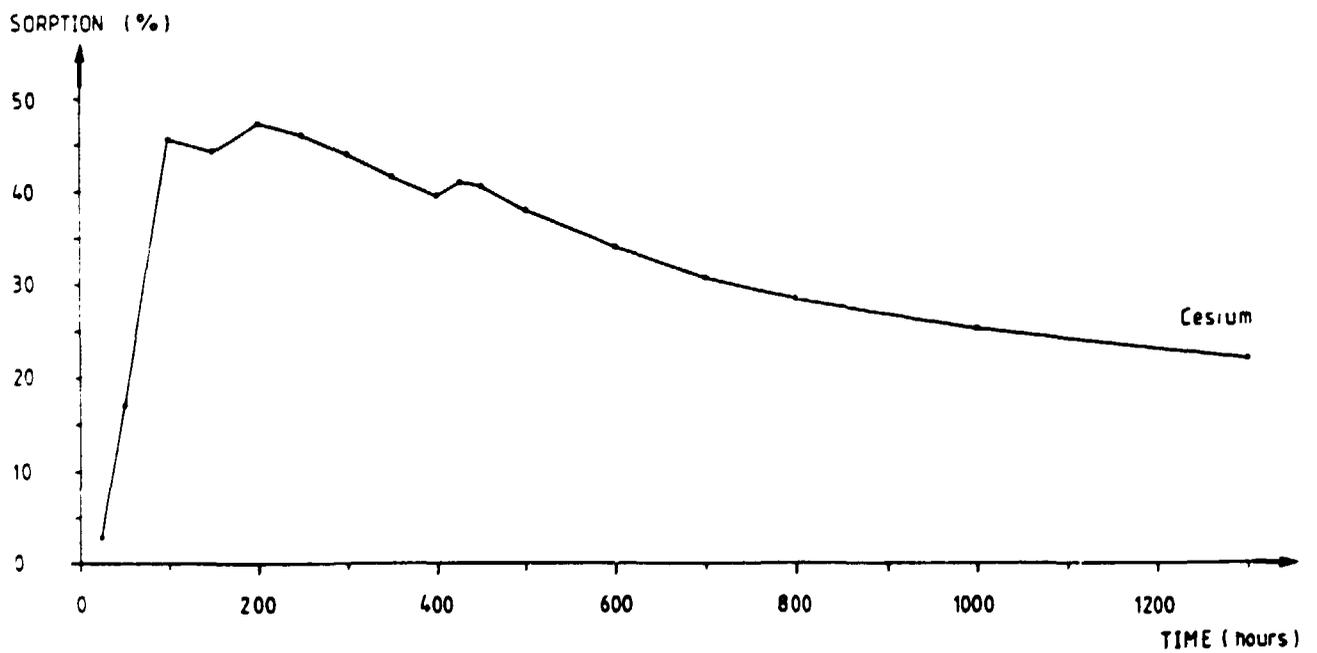
Fig. 5.2a Strontium sorption relative to iodide

Fig. 5.2b Cesium sorption relative to iodide

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