TECHNICAL
REPORT

87-22

Radionuclide sorption on granitic drill core material

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November 1987

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RADIONUCLIDE SORPTION ON GRANITIC DRILL CORE MATERIAL

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Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20) and 1986 (TR 86-31) is available through SKB.

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ABSTRACT

Distribution ratios (K_d) were determined for ^{85}Sr, ^{134}Cs and ^{152}Eu on crushed granite and fissure coating/filling material from Stripa mines. Measurements were also carried out on intact fissure surfaces. The experimental data for ^{85}Sr and ^{134}Cs on crushed material can be accomodated by a sorption model based on the assumption that the crushed material consists of porous spheres with outer and inner surfaces available for sorption. In the case of ^{152}Eu only sorption on the outer surfaces of the crushed material was observed.The absence of sorption on inner surfaces is most probably due to high depletion of the more strongly sorbed ^{152}Eu in the water phase and very low diffusivity of ^{152}Eu in the sorbed state .

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INTRODUCTION

Transport of radionuclides through granitic drill cores containing natural fissures has been subjected to several studies in our laboratories /1-5/

The models used to interpret the experimental data encompass hydrodynamic dispersion,channeling,diffusion into the rock matrix and sorption on the fissure sufaces and surfaces within the rock matrix.

Whereas the diffusion into the rock matrix in the long time perspective may create a high capacity sink for sorbed radionuclides sorption on the walls of the water carrying fissure most probably will be dominating in laboratory experiments with contact times in the time range minutes-hours.Understanding of the dynamics of the sorption processes is therefore of great importance in modelling the radionuclide transport in labotatory and field experiments.

Most of the sorption work on granitic rock has been carried out on crushed material and reported as Freundlich isotherms or distribution ratios R_d.

The latter is defined as

$$\frac{\text{amount of radionuclide sorbed/g dry material}}{\text{amount of radionuclide/cm}^3\text{ solution}}$$

To translate mass based R_d values into surface related R_a values assumptions about particle shape and size distribution of the size separated fractions of the crushed and sieved

material must be made. A fundamental question is whether crushing, leading to the creation of fresh fracture surfaces, modifies the sorption properties or not.
The aim of the present study is to compare sorption data from experiments with crushed and intact granitic drill core material respectively.

EXPERIMENTAL

The rock samples used in this study are granitic drill cores from the Stripa mine, taken at a depth of 360 m below the ground level.Granite and coating/filling material from natural fissures in the drill cores was crushed using a Agat mortar and pestle and size sorted by wet sieving into the size ranges given below.
The radionuclide solutions were prepared by dilution of acid stock solutions of ^{22}Na,^{85}Sr,^{134}Cs and ^{152}Eu (Amersham) with artificial groundwater synthesized to represent the natural water in contact with granitic rock (Table 1).

The cation exchange capacity (CEC) was measured by isotope dilution /6/ using ^{22}Na as tracer. 100 mg crushed rock was equilibrated for 48 hours with 3cm^3 0.5 mol.dm^{-3} NaCl solution spiked with ^{22}Na.The solution was thereafter vacuumfiltrated through a 0.5um polypropylene filter (Gelman) and the activity of the solid phase and the filtered solution measured with a (2-x 2 in)well type NaI detector connected to a 256 channel analyzer.

Distribution ratios (R_d): Samples containing 100 mg crushed and sieved material and 3 cm^3 groundwater were equilibrated in polypropylene tubes which were gently agitated. Tracers were added and the activity of the solid phase and solution monitored at regular time intervals by filtration and counting as described above.The radionuclide concentrations used were ^{85}Sr $2.5 \cdot 10^{-11}$,^{134}Cs $1.1 \cdot 10^{-9}$ and ^{152}Eu $5 \cdot 10^{-8}$ $mol \cdot dm^{-3}$.

Sorption on intact rock: 1.2 cm^2 areas of fissure surfaces consisting of granite and alteration products were sealed off and contacted with radionuclide solutions (Fig 1).After 48h the activity on each surface was measured with a planar (2 x 2in) NaI detector connected to a 256 channel analyzer.

SORPTION MODEL FOR CRUSHED MATERIAL

It is assumed that the crushed material consists of porous spherical particles /7/ with both outer and inner surfaces accessible for sorption. It is further assumed that the inner surface area is proportional to the particle volume.
The surface area/volume of a spherical particle with diameter d_p is given by the relationship

$$A_p/V_p = 6/d_p \qquad (1)$$

and the distribution ratio can thus be written

$$R_d = R_v + R_a\ (6/\rho \cdot d_p) \qquad (2)$$

where R_v denotes sorption on the inner surfaces per unit mass ($cm^3 \cdot g^{-1}$) R_a denotes sorption on the outer surface ($cm^3 \cdot cm^{-2}$) and ρ is the rock density (2.61 $g \cdot cm^{-3}$).

EXPERIMENTAL RESULTS

The surfaces of the water carrying fissures display a variation in light and darker coloured areas. Samples of the host rock and fissure filling material were studied by X-ray diffraction (XRD), sweeping electron microscopy (SEM) and differential thermal analysis (DTA/DTG).

The host material was found to have a normal granitic composition i.e. containing the minerals mica, feldspar, chlorite/biotite, quartz and traces of calcite.The light coloured fissure filling material was found to have a corresponding composition, probably with somewhat reduced quartz content.The dark (greenish) coloured fissure filling material was found to have lower quartz and higher chlorite content than the host rock.

The content of K,Mg and Fe was higher than in the host rock.

The cation exchange capacity of crushed material is, in accordance with the model described above (eqn 2),plotted versus $1/\bar{d}$ where $\bar{d}$ for each particle size fraction is taken to be the arithmetic mean of the apertures of the sieves bracketing the various size fractions /8/.The size fractions and d values are tabulated in Table 2.

With the notable exception of the smallest size fraction (63-125 μm) the experimental data display the expected linear 1/d dependence.

Typical R_d versus contact time plots for ^{85}Sr and ^{134}Cs sorption on crushed granite are shown in Fig 3. As can be gleaned from the plots the prompt sorption is followed by further sorption and the calculated R_d reach plateau values twice the prompt values within 72 hours.
The R_d values measured 1 minute and 48 hours respectively after addition of ^{85}Sr are plotted versus $1/\bar{d}$ in Fig 4. Corresponding plots for 48 hours sorption of ^{134}Cs on granite and fissure filling material are shown i Figs 5-7.
It should be noted that all the experimental data plotted in Figs 2-7 indicate that the assumtion of porous particles is reasonable.
Corresponding plots ,in Figs 8-10, for the ^{152}Eu sorption also give a linear dependence of R_d on $1/\bar{d}$ but in this case the fitted straight lines pass through or very close to origo indicating a very slight if any volume effect.

DISCUSSION

The cationic exchange capacities and distribution ratios calculated using eqn 2 are summarized in Tables 3 and 4 respectively.

If it is assumed that sorption on the crushed material is governed only by the availability of internal and external surfaces i.e. with no differences in sorption properties the CEC_a /CEC_v and R_a/R_d ratios,for each material (host rock or fissure filling), should be the same for the radionuclides studied. For granite this ratio is found to be 0.013,0.007 and 0.0082 for ^{22}Na,^{85}Sr and ^{134}Cs respectively. The variation is within the experimental errors. It should be noted that the CEC_a values obtained from experiments with intact surfaces (12 hours contact time) are in fair agreement with the corresponding value calculated from the plot in Fig 2. The R_a value measured after 48 hours sorption of ^{134}Cs on intact fissure surfaces is however at least one order of magnitude higher than the corresponding values obtained from Figs 5-7. As mentioned above, for ^{152} Eu the R_d versus $1/\bar{d}$ plots for 48 hours contact time give no evidence for sorption on surfaces within the particles.Furthermore the R_a value obtained in experiments with intact fissure surfaces is in good agreement with the results from experiments with crushed material.

The experimental results for the radionuclides used in this investigation can be fairly well accomodated by the simple porous sphere model. The moderately sorbed strontium and more strongly sorbed cesium ions have been shown to display high diffusivities in compacted bentonite / 9/ ,granitic rock /10/ and sandstone /11/ and, according to the experimental data in this investigation, sorption equilibria are reached on all surfaces within 72 hours for 63-1200 μm particles. The high R_a

value obtained for for ^{134}Cs sorption on intact fissure surfaces is probably due to diffusion into the rock matrix. ^{152}Eu ,the most strongly sorbed radionuclide, is most probably like cobalt and americium /12/ highly immobilized upon sorption. Moreover,due to the strong sorption the radionuclide concentration in the water phase is very low and the migration of ^{152}Eu into the porous particles and rock matrix might be expected to be very slow.This is also evidenced by the good agreement between the R_a values obtained in experiments with crushed material and intact fissure surfaces. The time required to reach sorption equilibrium on inner as well as outer particle surfaces will therefore be very long and the experimentally determined R_d values are only a measure of the sorption on the outer surfaces and not of the sorption capacities of the crushed material.

CONCLUSIONS

1. Equilibria for sorption of the cations Sr^{2+} and Cs^{+} on crushed granite and fissure filling material are reached within 3-4 days for particles with 63-2000 μm diameter.
The experimental data indicate that the crushed material can be treated as consisting of porous spheres with inner and outer surfaces accessible for sorption.

2. No volume effect is observed for the strongly sorbed ^{152}Eu which is highly immobilized in its sorbed state. Moreover the radionuclide concentration in the water phase is very low due to the strong sorption. To obtain redistribution of the promptly sorbed ^{152}Eu on the outer surfaces, which is required to obtain a measure of the sorption capacity of the crushed material, will therefore require long term experiments.

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Table 1.

Composition of artificial groundwater.[a)]

Species	Concentration $mg \cdot dm^{-3}$	Species	Concentration $mg \cdot dm^{-3}$
HCO_3^-	123	Ca^{2+}	18
SO_4^{2-}	9.6	Mg^{2+}	4.3
Cl^-	70	K^+	3.9
SiO_2	12	Na^+	65

a) pH 8-8.2, Eh 260mV (aerated)

Table 2.

Size fractions of crushed material used,

Size fraction μm	$1/\bar{d}$ cm^{-1}
63-125	106.4
125-250	53.3
250-500	26.7
250-750	20.0
500-750	16.0
750-1000	11.4
1000 -2000	6.7

Table 3.

Cationic exchange capacities.

Material	CEC_v µequiv·g^{-1}	CEC_a µequiv·cm^{-2}
crushed granite	17± 3.2	0.22 ± 0.1
granite surface a)		0.24 ± 0.2
light coloured a) fissure filling		0.45 ± 0.2
dark coloured a) fissure filling		0.77 ± 0.25

a) contact time approx 12 hours

Table 4.

Distribution ratios calculated from Figs 4-11 using the equation $R_d = R_v + (6/\rho\cdot\bar{d})R_a$

Material	Nuclide	R_v $cm^3\cdot g^{-1}$	R_a $cm^3\cdot cm^{-2}$
granite	^{85}Sr	5.1 ± 0.3	0.032 ± 0.005
	^{134}Cs	33 ±5	0.27 ±0.04
	^{152}Eu		4.6 ± 0.1
light coloured fissure filling	^{134}Cs	52 ± 3	0.87 ± 0.07
	^{152}Eu		3.5 ± 0.23
dark coloured fissure filling	^{134}Cs	31 ± 2.3	0.98 ± 0.02
	^{152}Eu		3.95 ± 0.13
intact fissure surface	^{134}Cs		6.4 ± 0.
	^{152}Eu		4.5 ± 0.5

FIGURE LEGENDS

Fig 1. Experimental arrangement for measuring radionuclide sorption on intact fissure surfaces.

Fig 2. Cationic exchange capacity (CEC) of crushed granite plotted vs $1/\bar{d}$. ($\bar{d}$ is the mean diameter of the particle size fraction).

Fig 3. R_d for sorption of ^{85}Sr and ^{134}Cs on crushed granite plotted vs time of contact.

○ ^{85}Sr 125-250 µm, left hand scale
□ ^{85}Sr 1000-2000 µm, left hand scale
▽ ^{134}Cs 63-125 µm, right hand scale

Fig 4. R_d for sorption of ^{85}Sr on crushed granite plotted vs $1/\bar{d}$.($\bar{d}$ is mean diameter of particle size fraction
▽ 1-2 min contact time
○ 48 h contact time

Fig 5. R_d for sorption of ^{134} Cs on crushed granite plotted vs $1/\bar{d}$.($\bar{d}$ is mean diameter of particle size fraction) 48 h contact time.

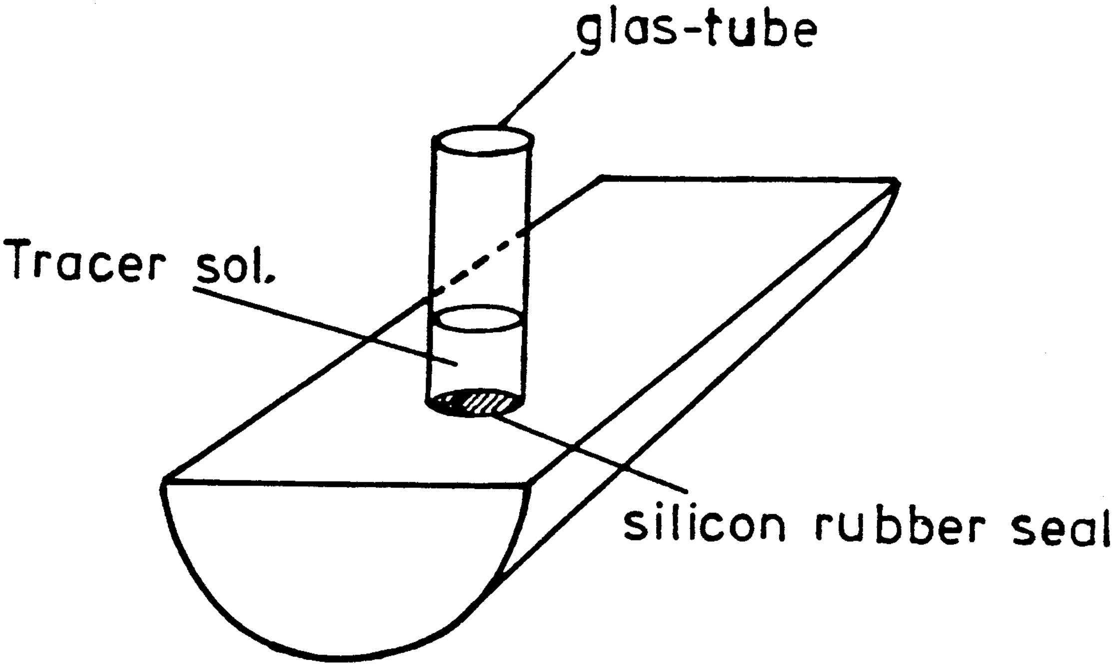
Fig 6. R_d for sorption of ^{134}Cs on crushed light coloured fissure filling plotted vs $1/\bar{d}$.($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

Fig 7. R_d for sorption of ^{134}Cs on crushed dark coloured fissure filling plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

Fig 8. R_d for ^{152}Eu sorption on crushed granite plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

Fig 9. R_d for ^{152}Eu sorption on crushed light coloured fissure filling plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

Fig 10. R_d for ^{152}Eu sorption on crushed dark coloured fissure filling plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.



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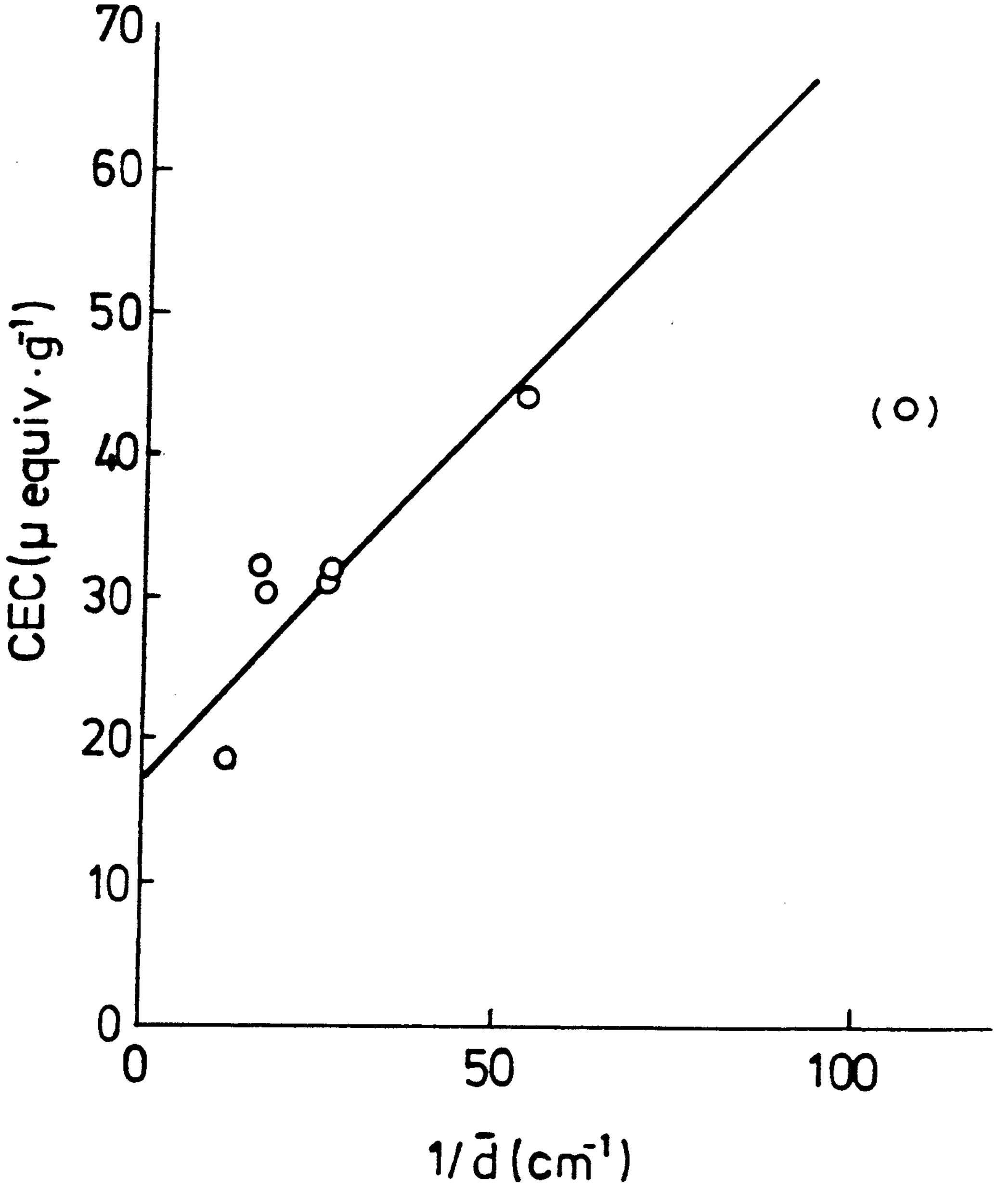

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($\bar{d}$ is the mean diameter of the particle size fraction).

Fig 3.. R_d for sorption of ^{85}Sr and ^{134}Cs on crushed granite plotted vs time of contact.

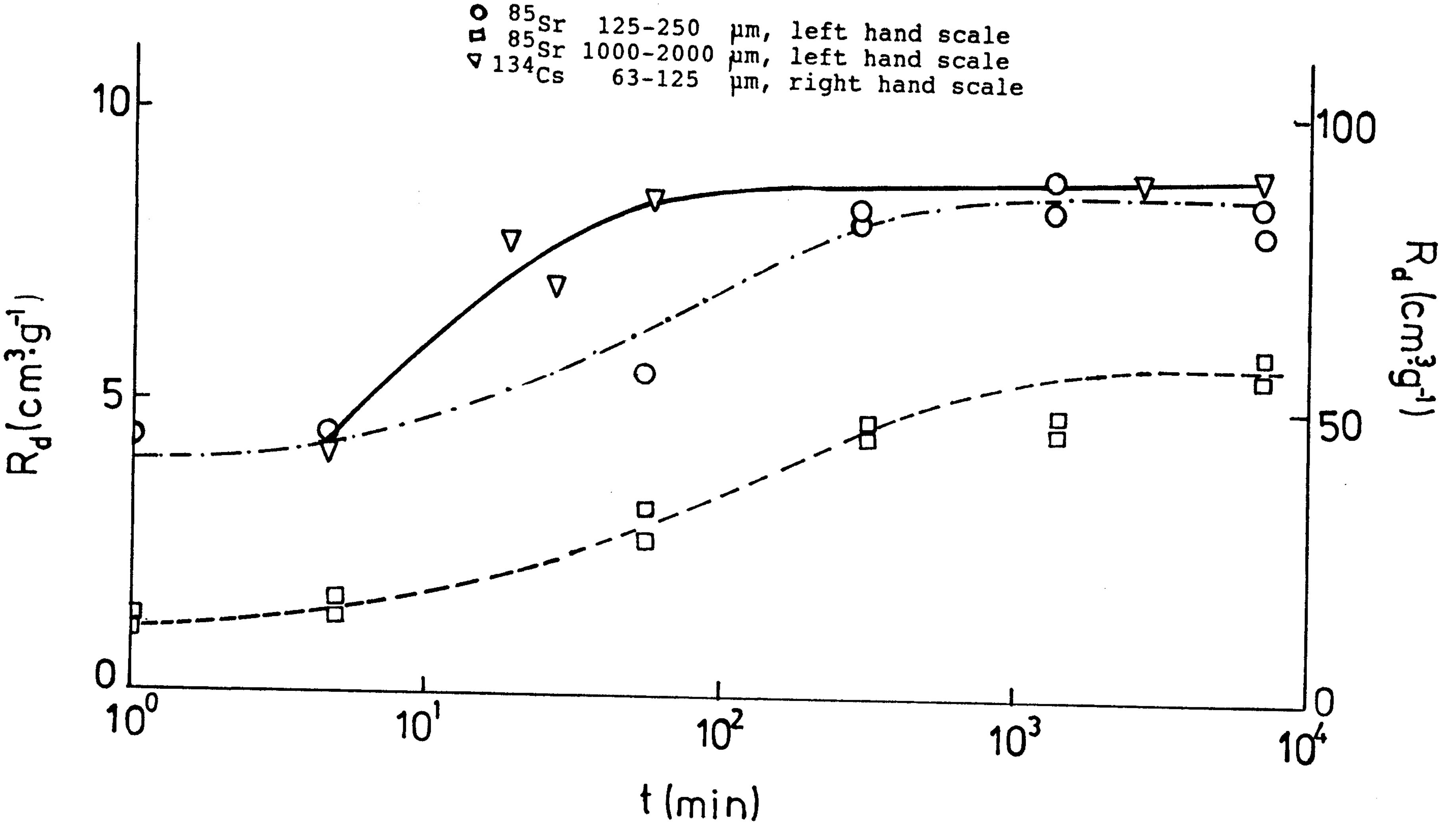

Fig. 3

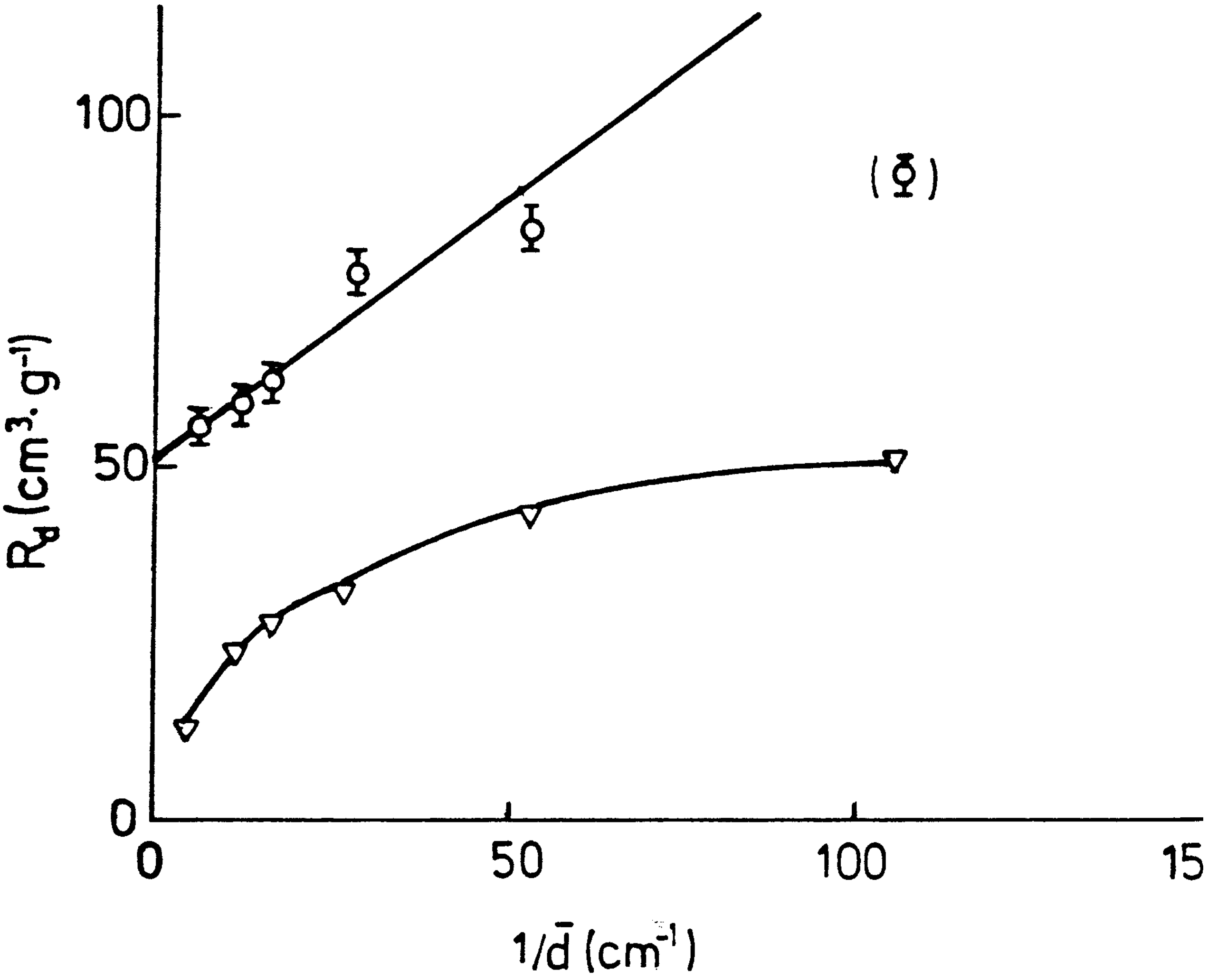

Fig 4. R_d for sorption of ^{85}Sr on crushed granite plotted vs 1/d̄. (d̄ is mean diameter of particle size fraction

▽ 1-2 min contact time

○ 48 h contact time

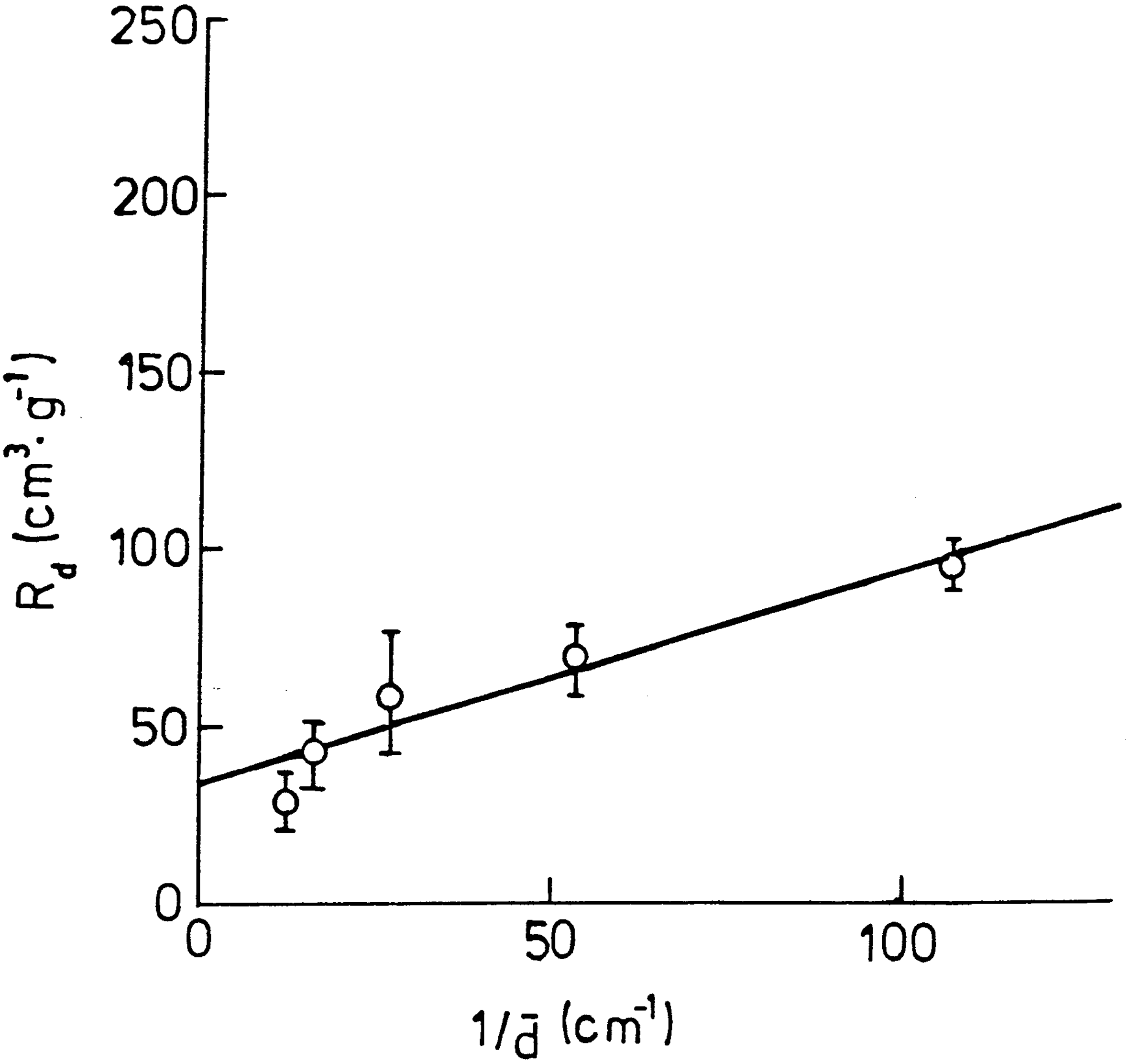

Fig 5. R_d for sorption of ^{134}Cs on crushed granite plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction) 48 h contact time.

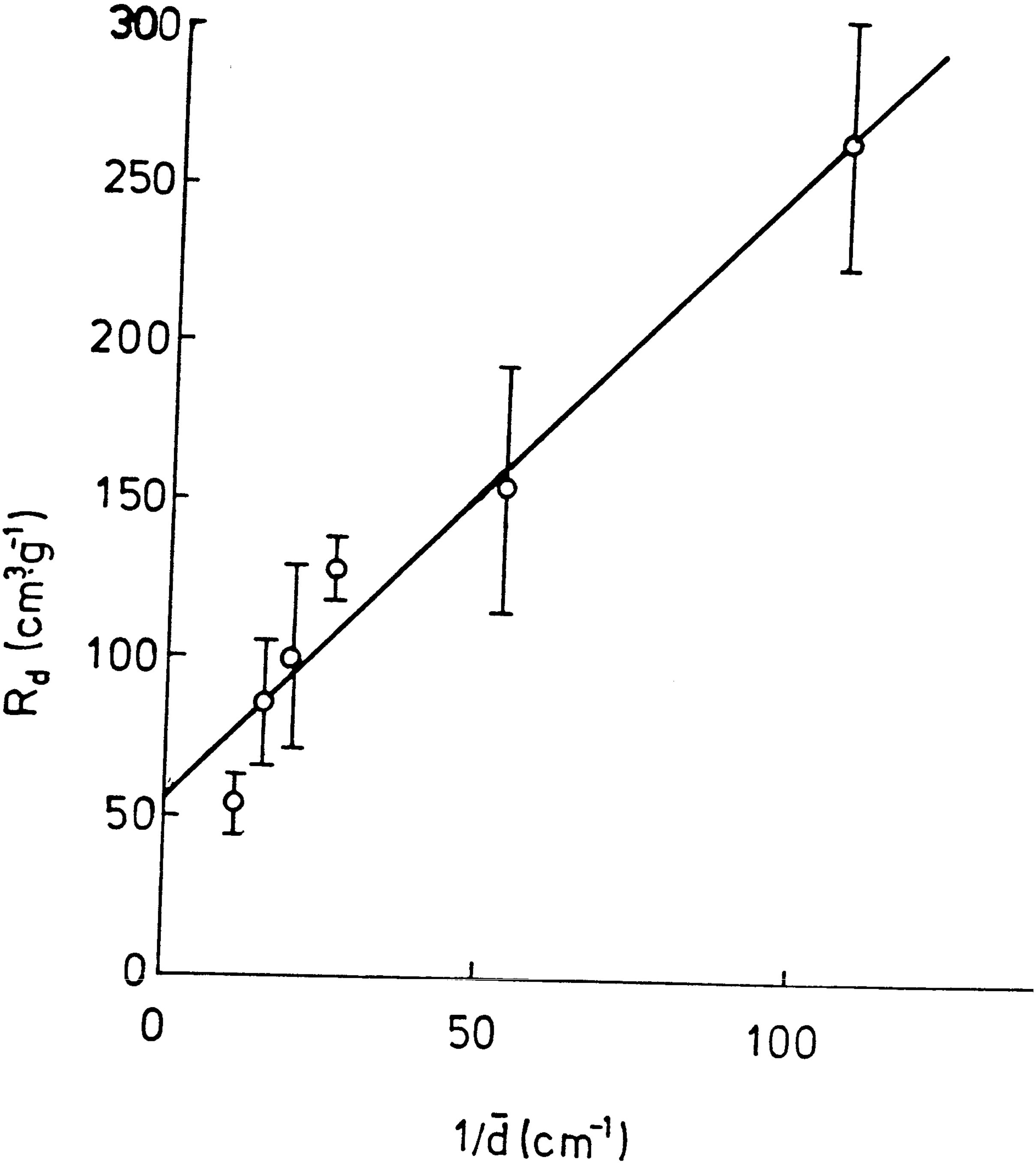

Fig 6. R_d for sorption of ^{134}Cs on crushed light coloured fissure filling plotted vs 1/$\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

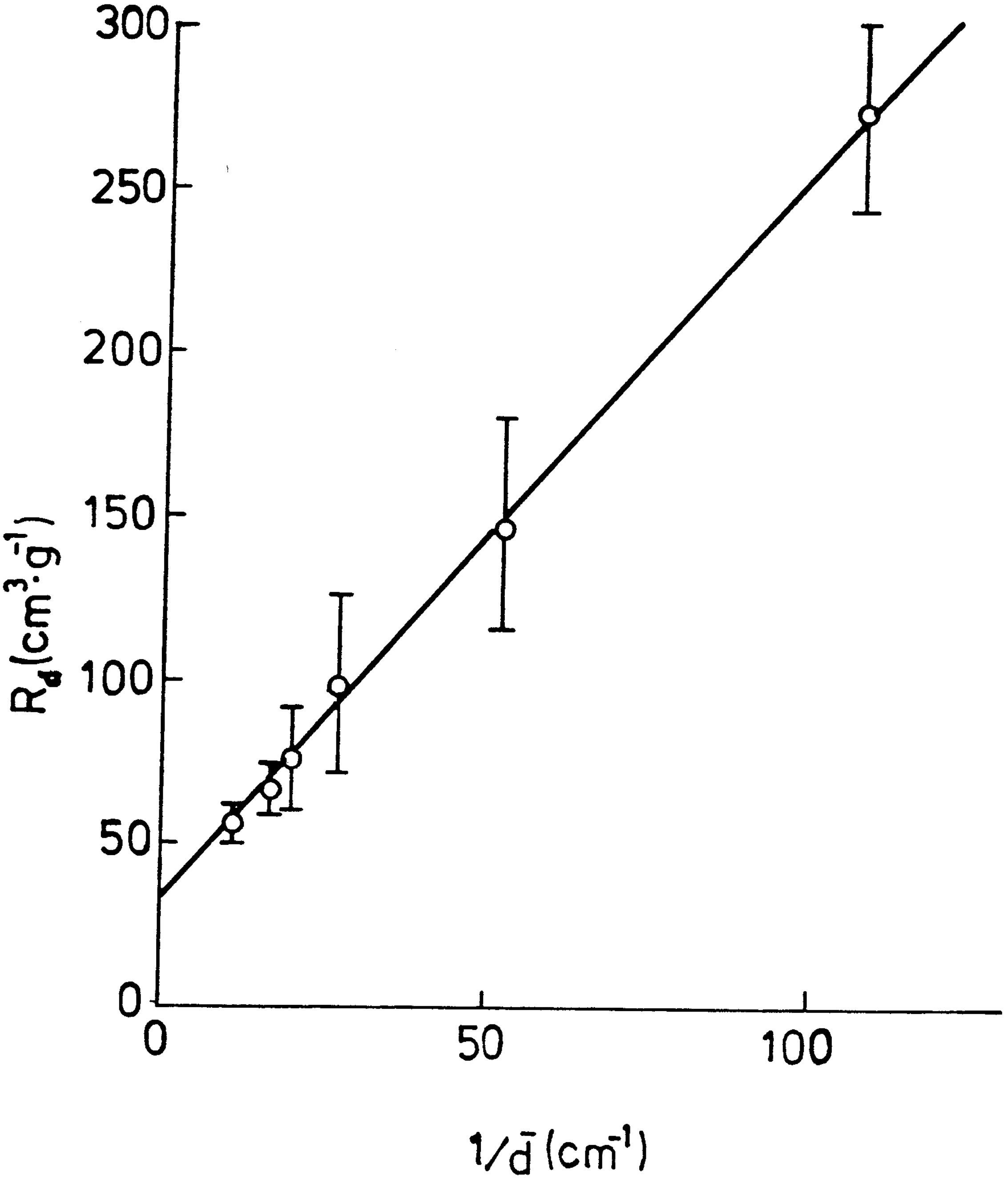

Fig 7. R_d for sorption of ^{134}Cs on crushed dark coloured fissure filling plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

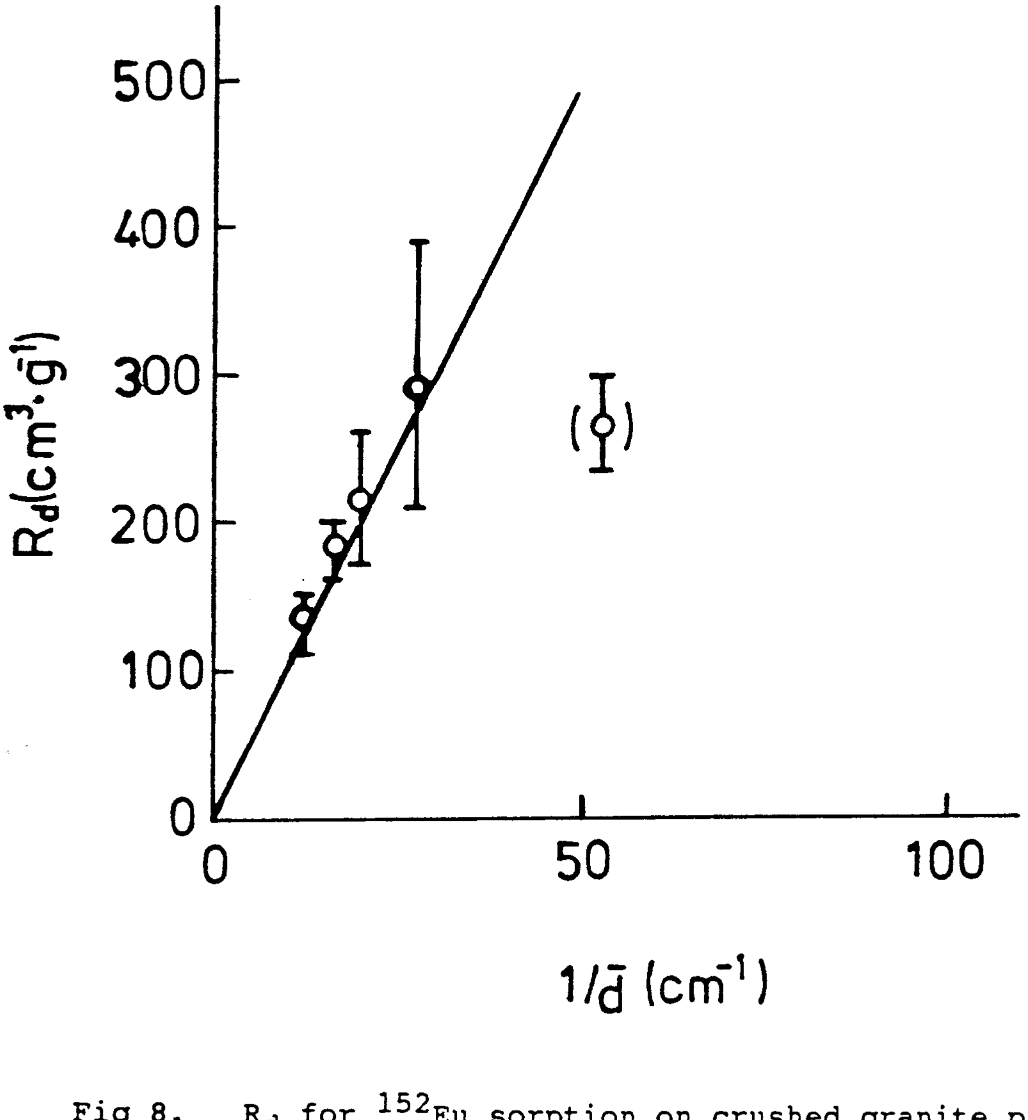

Fig 8. R_d for ^{152}Eu sorption on crushed granite plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

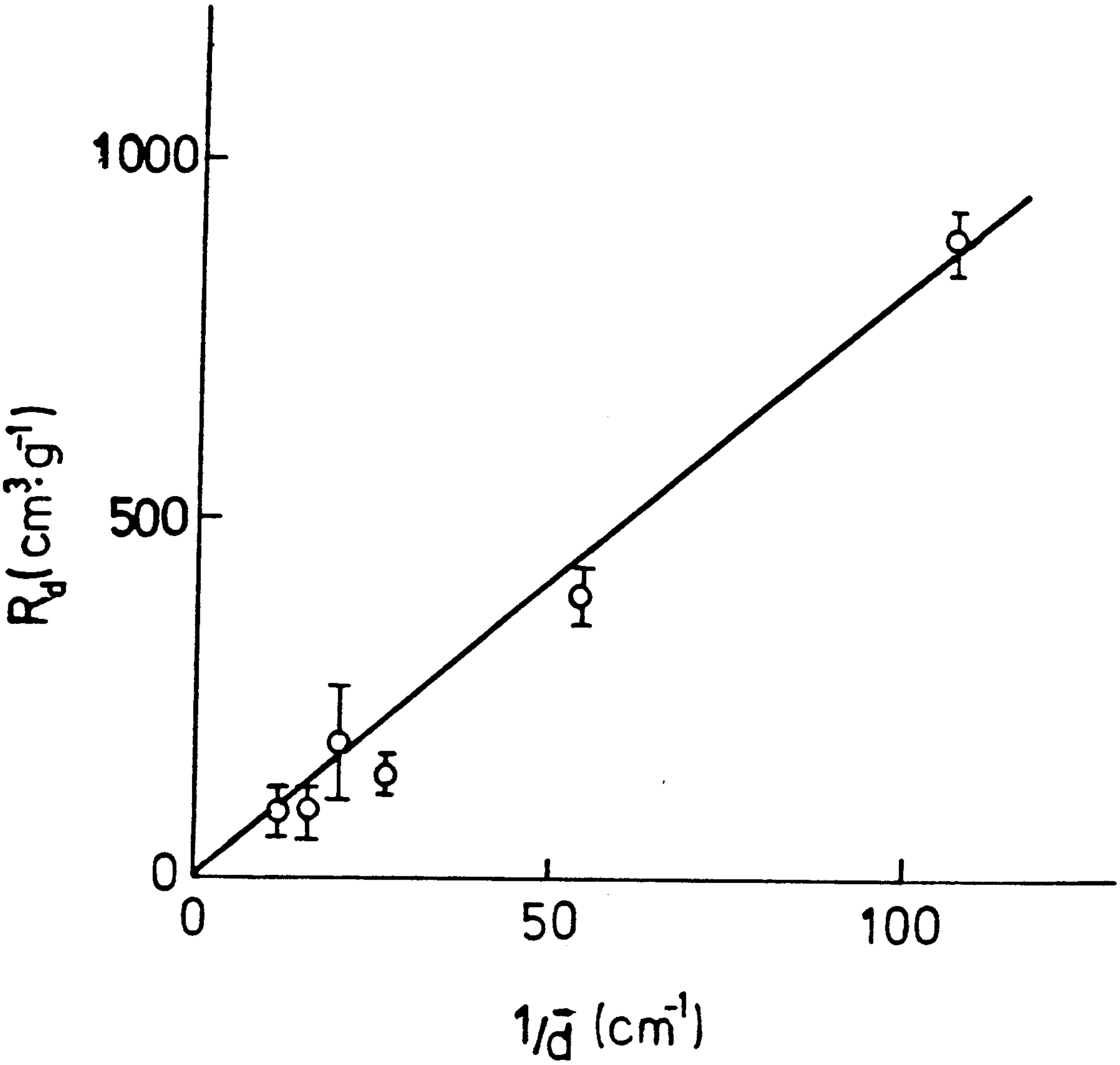

Fig 9. R_d for ^{152}Eu sorption on crushed light coloured fissure filling plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

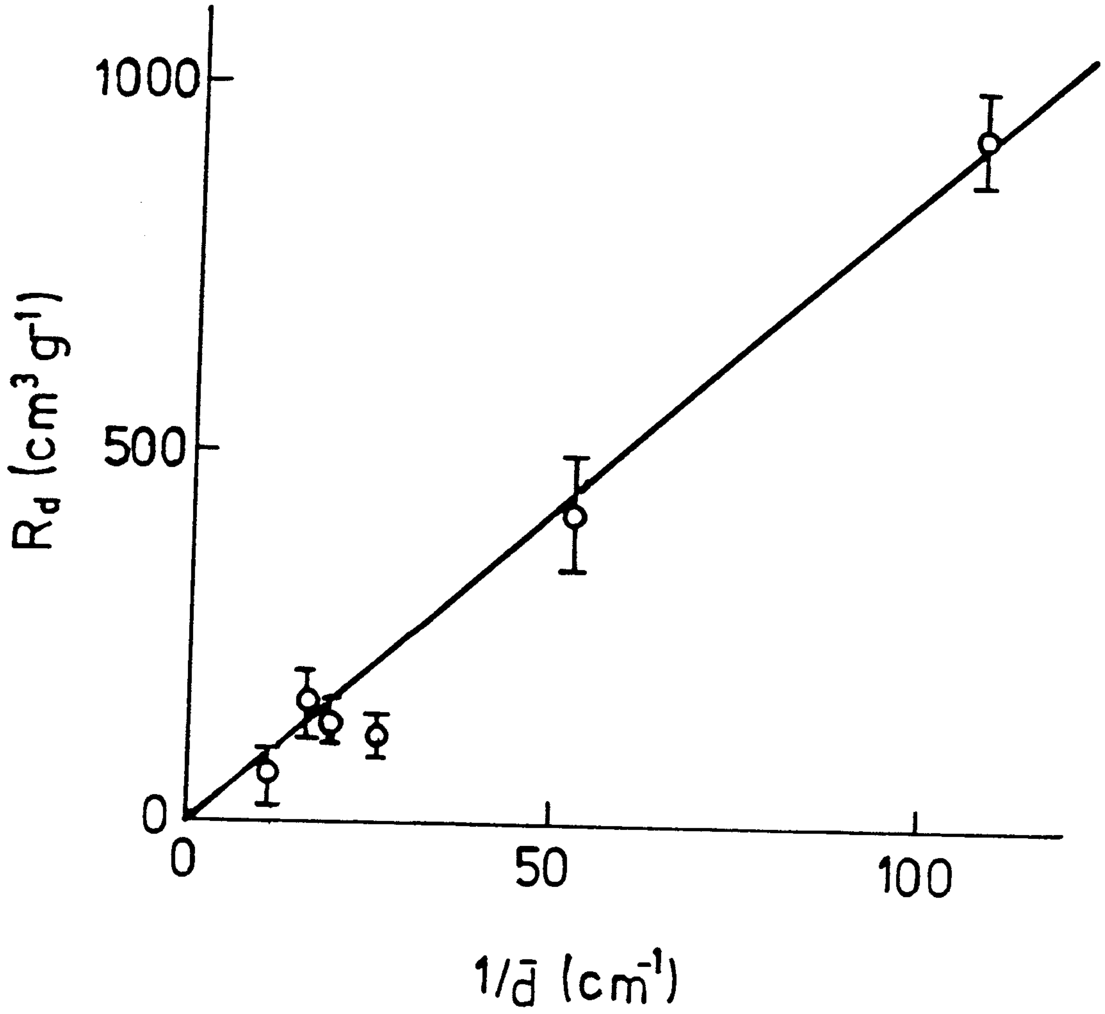

Fig 10. R_d for ^{152}Eu sorption on crushed dark coloured fissure filling plotted vs $1/\bar{d}$. ($\bar{d}$ is mean diameter of particle size fraction). 48 h contact time.

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[2]The Swedish Nuclear Fuel and Waste Management Co (SKB), Stockholm, Sweden
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September 1987

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Calculation of gas migration in fractured rock – a continuum approach

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September 1987

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September 1987