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Ion diffusion in compacted sodium and calcium bentonites

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A list of other reports published in this series during 1981, is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28) and 1980 (TR 80-26) is available through SKBF/KBS.

Summary.

The diffusivities of Sr^{2+} and Cs^{+} in compacted Erbslöh Ca-bentonite and Mx-80 Na-bentonite have been determined by various tracer techniques. Whereas the diffusivity of Sr^{2+} was found to be $(1,5 \pm 0,2) \cdot 10^{-11}$ $m^{2} \cdot sec^{-1}$ in both bentonites the diffusivity of Cs^{+} was found to be $(7 \pm 2) \cdot 10^{-13}$ and $(2.5 \pm 0,5) \cdot 10^{-12}$ $m^{2} \cdot sec^{-1}$ in Erbslöh and Mx-80 respectively. A comparison of the diffusivities of Sr^{2+} and Cs^{+} with the diffusivities of Cl^{-} and I^{-} earlier obtained shows that high K_d-values are not necessarily an indication of immobilization i.e. a simple pore diffusion model with retardation of the diffusing ions by sorption processes is not valid for Sr^{2+} and Cs^{+}. Water ratio (density) and homogenization time were not found to have any measurable effect on the diffusivity of the cations.

Introduction.

The KBS concept concerning the storage of nuclear fuel wastes implies that canisters be deposited in drilled holes and isolated from the rock by a clay barrier consisting of highly compacted bentonite. The bentonite is not fully water saturated at its deposition. Hence it will take up additional water from the rock, swell and thereby a perfect contact between the clay and rock might be created.

The clay is assumed to create a first barrier for the transport of radionuclides from leaking canisters and several studies of the diffusion of tracer nuclides through compacted clay have therefore been carried out.

In an early study Neretnieks et al (1) measured the transport of Cs^+ and Sr^{2+} from an aqueous solution into a compacted bentonite cylinder. The interpretation of the experimental data was based on the pore diffusion model which implies that the migration takes place in the pore water and that the ions are retarded by sorption processes. Hence very low effective diffusivities were obtained. Low values were also obtained for Ag^+ in a study by Allard et al (2).

In our previous study (3) higher diffusivities than expected were obtained for Cs^+ and Sr^{2+} and lower than expected for I^- and Cl^-. In a recent paper Allard et al (4) also obtained higher diffusivities than expected for Cs^+ and Sr^{2+} and concluded that the diffusion of ions through the compacted clay takes place by two processes.

In our previous study the radionuclides were allowed to diffuse into the bentonite cylinders through steel filters creating an interface between the radionuclide containing solution and the bentonite. To avoid the use of filters, being a source of error, new swelling oedometers were constructed. The alternative use of a calcium rich instead of a sodium rich bentonite has been discussed for other radioactive waste storage concepts (low and medium level wastes). Due to the interaction between bentonite and ground water and other waste storage components (i.e. concrete in the low and medium level wastes concepts) ion exchange will probably take place and thereby to a certain degree change the calcium/sodium content of the clay. Therefore a calcium rich as well as a sodium rich bentonite are included in this work. To study the effect of differing water ratio experiments have been carried out with calcium bentonite at two densites 2,1 and 1,6 ton·m^{-3}.

Equipments and clay preparation.

The experiments were carried out in swelling oedometers constructed at the University of Luleå especially for the purpose (see fig. 1). Bentonite was compacted to desired density and thereafter contacted with water. The water saturation is completed after a few days whereas the homogenization is a very slow process. The samples were therefore rested for varying periods before the diffusion started. All experiments were carried out at 25^{o}C in thermostated boxes.

Materials, solutions.

Two commercially available bentonites were used: the American Colloid Co type MX-80 granulated Na-bentonite and the Bavarian Erbslöh Ca-bentonite. The water saturation of the bentonite samples was made by means of the KBS reference water "Allard's" solution (cf KBS report 98) which is a synthetic ground water. The radionuclides were obtained in aqueous stock solution as follows: ^{85}Sr in 0,5 M HCl, ^{134}Cs as CsCl. ^{85}Sr and ^{134}Cs were selected as tracers because they are γ-emitters and can easily be analyzed without the need of chemical separation. Tracer solutions were prepared by diluting small aliquots (μl) of the stock solutions with Allard water.

Tracer methods.

To obtain a well defined tracer distribution before the start of the diffusion experiments two techniques were used.

I. Tracers were added to the water equilibrated with the 8-15 mm thick bentonite cylinder in cell A for at least 2-3 weeks. The cells A and B were opened and thereafter mounted as shown in figure 1. By this prodecure an extended source of limited extent was obtained.

II. Tracers were added to the water in contact with the upper surface of the bentonite cylinder in cell B. Continuous circulation was applied for a few hours. Due to the high K_d-values (cf. KBS-report 81-06) the radionuclides used were enriched on the surface of the bentonite. The cells A and B were opened and thereafter mounted as shown in figure 1. If the mean displacement during diffusion is much greater than the initial layer thickness,
i.e. t(diff) >>t(radionuclide contact),the activity distribution can be regarded as an impulse-source.

The oedometers were opened 10-20 days after the onset of diffusion and the cylindrical bentonite specimens sliced into 0,5-2 mm thick discs. The discs were weighted and their radionuclide content measured with a 3" x 3" NaI well type scintillation detector connected to a 256 channel pulse height analyzer. In some cases the activity measurements were carried out with a GeLi detector connected to a 4000 channel pulse height analyzer. Counting data were corrected for background radiation and in the case of ^{85}Sr also for the interference of ^{134}Cs decay. After γ-counting the bentonite samples were dried and the water content determined. The water ratio was found to be constant throughout the volume of each bentonite cylinder.

Evaluation of diffusion coefficients.

I. Extended source of limited extension: the diffusion coefficients were calculated by fitting the experimental data to the equation (5).

$$c/co = \frac{1}{2}\left[\operatorname{erf}\frac{1-x/h}{2/h\cdot(Dt)^{1/2}} + \operatorname{erf}\frac{1+x/h}{2/h\cdot(Dt)^{1/2}}\right] \qquad (1)$$

where c = tracer concentration at distance x from surface.

c_0 = tracer concentration in radionuclide containing volume at $t = 0$.

h = thickness of radionuclide containing bentonite cylinder.

t = time after onset of diffusion.

D = diffusivity.

II. Impulse source.
The experimental data were fitted to the equation (5).

$$c/N = \frac{1}{2\cdot A(\pi\ Dt)^{1/2}}\, e^{-x^2/4Dt} \qquad (2)$$

where c = tracer concentration at distance x from the plane impulse source.

N = total amount of tracer in impulse source.

A = area of contact surfaces.

t = time after onset of diffusion.

D = diffusivity.

Results.

Figures 2-5 illustrate typical distributions of Sr^{2+} and Cs^{+} after diffusion from an extended source of limited extent

Table 1.

Diffusion coefficients for Sr^{2+} and Cs^{+} calculated from concentration profile analyses.

Series	Bentonite	Density ton·m^{-3}	Homogenization time (weeks)	D $m^2 \cdot sec^{-1}$ Sr^{2+}	Cs^{+}	Exp.cond.
11	MX-80	2.1	3	$1.4 \cdot 10^{-11}$	$2 \cdot 10^{-12}$	I
7	MX-80	2.1	9	$1.4 \cdot 10^{-11}$	$3 \cdot 10^{-12}$	I
8	MX-80	2.1	9	$1.5 \cdot 10^{-11}$	$2.5 \cdot 10^{-12}$	I
9	MX-80	2.1	9	-	$2.8 \cdot 10^{-12}$	Ic
3	MX-80	2.1	29	$8 \cdot 10^{-12}$		IIa
4	MX-80	2.1	29	$1 \cdot 10^{-11}$	$1.5 \cdot 10^{-12}$	II
10	Erbslöh	1.6	3	$7 \cdot 10^{-12}$	-	Ia
14	Erbslöh	2.1	9	$1.3 \cdot 10^{-11}$	$6 \cdot 10^{-13}$	II
5	Erbslöh	1.6	9	$1.3 \cdot 10^{-11}$		Ib
6	Erbslöh	1.6	9	$1.2 \cdot 10^{-11}$		Ib
12	Erbslöh	1.59	14	$3.2 \cdot 10^{-11}$	$6 \cdot 10^{-13}$	I,II
1	Erbslöh	1.57	29	$1.5 \cdot 10^{-11}$	$7.5 \cdot 10^{-13}$	II
2	Erbslöh	1.59	29	$1.6 \cdot 10^{-11}$	$7.0 \cdot 10^{-13}$	II

I - extended source

II - plane pulse source

a - somewhat skewed distribution indicates bad surface contact, i.e. computed diffusion coefficient probably sligthly too low

b - ^{85}Sr distribution only analyzed, due to low $^{134}Cs^{+}$ concentration

c - samples containing $^{134}Cs^{+}$ only (case I). The theoretical distributions are given by the dotted lines. Corresponding distributions for diffusion from an instantaneous plane source are demonstrated in Figures 6-8.

The experimental conditions and evaluated diffusion coefficients are given in Table 1. Concerning the accuracy of the diffusion coefficients it should be borne in mind that bentonite is a clay containing different minerals, montmorillonite beeing the main component. A certain variation between different qualities is to be expected and might cause some variation in the experimentally determined diffusivities.

In earlier experiments diffusion coefficients were calculated from concentration profiles obtained after 10 days contact between bentonite cylinders and aqueous tracer solutions. The diffusion coefficients from these experiments (KBS report 81-06) are given for comparison in Table 2.

Table 2.
Diffusion coefficients at 25^{o}C for Sr^{2+}, Cs^{+}, I^{-} and Cl^{-} calculated from concentration profile analyses (a) and steady state transport (b) (KBS report 81-06).

	Density	Diffusion coefficients $m^{2}\cdot sec^{-1}$				
Bentonite	ton·m^{-3}	Sr^{2+}	Cs^{+}	Cl^{-}	I^{-}	Method
MX-80	2.1	$2.3\cdot10^{-11}$	$7.5\cdot10^{-12}$	$6\cdot10^{-12}$	$4\cdot10^{-12}$	(a)
Erbslöh	2.1	$4.8\cdot10^{-11}$	$3.4\cdot10^{-12}$	-	$1\cdot10^{-12}$	(a)
MX-80	2.1			$3.1\cdot10^{-13}$	$2.1\cdot10^{-13}$	(b)
Erbslöh	2.1				$1.3\cdot10^{-13}$	(b)

Discussion.

The diffusivities obtained for Sr^{2+} and Cs^+, by the techniques described above, show the same pattern as obtained by concentration profile analysis in our earlier experiments but the calculated diffusivities are somewhat lower. This decrease in measured diffusivity, which is due to the effect of filter resistance in the previous diffusion experiments, was predicted in the discussion of KBS-report 81-06.

The diffusivity of Sr^{2+} is of the same order of magnitude as obtained by Ellis et al (6) for divalent cations in thin oriented clay films of montmorillonite. In the present work the density, and thereby the water ratio, of the Erbslöh-Ca bentonite as well as the time after the onset of water saturation of both bentonites were varied to study the effect of possible slow homogenization processes.

As can be seen from Table 2 no systematic changes in diffusivity are found within the experimental errors. As seen from Tables 1 and 2 the diffusivity of I^- and Cs^+ (and probably also Cl^-) is lower in Erbslöh than in MX-80. Whereas the diffusivities of Sr^+ and Cs^+ in our previous study were predicted to be too high due to filter resistance no such effect is expected for I^- and Cl^-. The diffusivities can therefore by arranged in order of magnitude.

$$D_{Sr^{2+}} > D_{Cl^-} > D_{I^-} \geq D_{Cs^+}$$

Although the diffusivities obtained are about two orders of magnitude lower than the diffusivities in water our data can clearly not be accommodated by a pore diffusion model according to which the migration takes place in the pore water and that the ions are retarded by sorption processes. A more probable model can be derived, as suggested in report 81-06, by regarding the compacted bentonite as an ion exchange membrane. The high cation exchange capacity and low anion capacity (∼70 and ∼5 meqv per 100 g dry bentonite respetively) of the bentonites indicate a clay framework with excess negative charge and high concentration of exchangeable counterions (cations) to preserve electroneutrality.

As seen from Table 2 the diffusion coefficients for Cl^- and I obtained from steady state transport are at least one order of magnitude lower than the diffusion coefficients calculated from concentration profile analyses.

This difference in diffusivity can, however, be explained if the assumption is made that the diffusion takes place in the pores containing a concentrated aqueous solution of the counterions. The steady state transport through a bentonite disc is thus described by the equation

$$N_f = -A \cdot \varepsilon_p \cdot D_f \cdot \frac{\delta_p}{\tau^2} \cdot \frac{\partial c}{\partial x} = -A \cdot \varepsilon_p \cdot D_p \cdot \frac{\partial c}{\partial x} \qquad (3)$$

where D_f is the diffusivity in solution.
D_p is the diffusivity in pores.
ε_p is the porosity.
δ_p is constrictivity of pores.
τ^2 is tortuosity of pores.
c is the concentration.
X is the thickness of bentonite disc
N_f is the flowrate of diffusing species.

The diffusion coefficients given in Table 2 were calculated using the geometrical area of the bentonite disc and should therefore be a factor ε_p smaller than the diffusion coefficients calculated from concentration profile analysis data as these experiments give a direct measure of $D_p = D_f \cdot \delta_p/\tau^2$.

The porosity of the bentonites used is about 0,3 and the diffusivity obtained in a steady state experiment should therefore be about a factor three lower than the diffusivity calculated from concentration analysis data. In the case of I^- in MX-80 the diffusivity ratio is however found to be $2{,}1\cdot10^{-13}/4\cdot10^{-12} \sim 1/20$. The reason for this difference is the low anion exhange capacity which causes the concentration of freely moving anions such as Cl^- and I^- to be very low in the bentonite. The concentration of Sr^{2+} and Cs^+ should on the other hand be high.

The concentration profiles in steady state transport experiments can therefore be described schematically as in Figure 9.

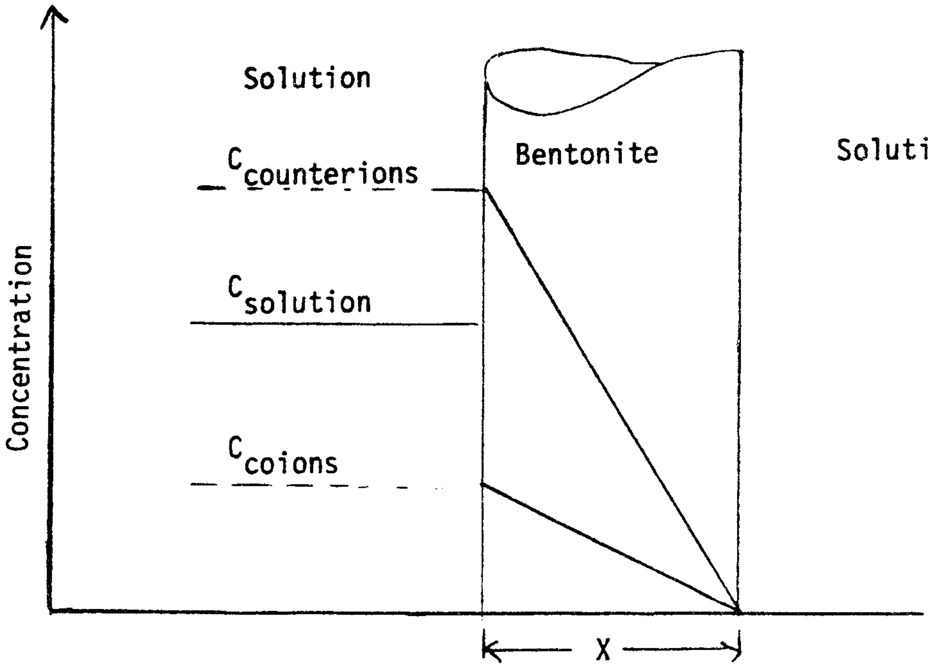

Figure 9

From the diffusivities obtained in Cl^-, I^- experiments and equation 3 the concentration gradients across the bentonite discs are estimated to be ∿ 15% of the concentration gradients calculated from the concentrations in the solutions on both sides of the bentonite discs. This is in very good agreement with the I^-, Cl^- concentration data obtained from analyses of the I^-, Cl^- content in the bentonite discs (report 81-06).

Conclusions.

The most important conclusion to be drawn from our data is that high K_d-values are not necessarily an indication of immobilization. The radii of the hydrated ions as given by Mark (8) are Sr^{2+} 2.74 Å; Cs^+ 1.47 Å; Cl^- 1.84 Å; I^- 2.16 Å. Although the absolute values of the ionic radii are somewhat uncertain, the order magnitude for the diffusivities in water should be

$$D_{Sr^{2+}} < D_{I^-} < D_{Cl^-} < D_{Cs^+}$$

The experimentally determined diffusivities as given in Tables 1 and 2, can therefore not be accommodated by a model in which the hydrated ions are free to move in an aqueous phase. It therefore seems probable that the ions move through the clay fully or at least partly stripped of their hydration shells. The main factor determining the diffusivity should therefore be the ionic size. Due to the low concentration of coions the transport capacity for anions will be very low as demonstrated by the small transport of Cl^- and I^- ions through bentonite in the steady state experiments.

Differing water ratio (density) and homogenization time were not found to have any measurable effect in the diffusion experiments.

Acknowledgements.

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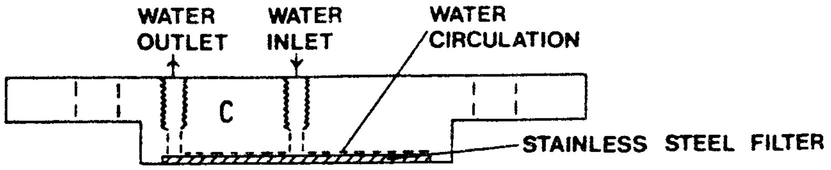
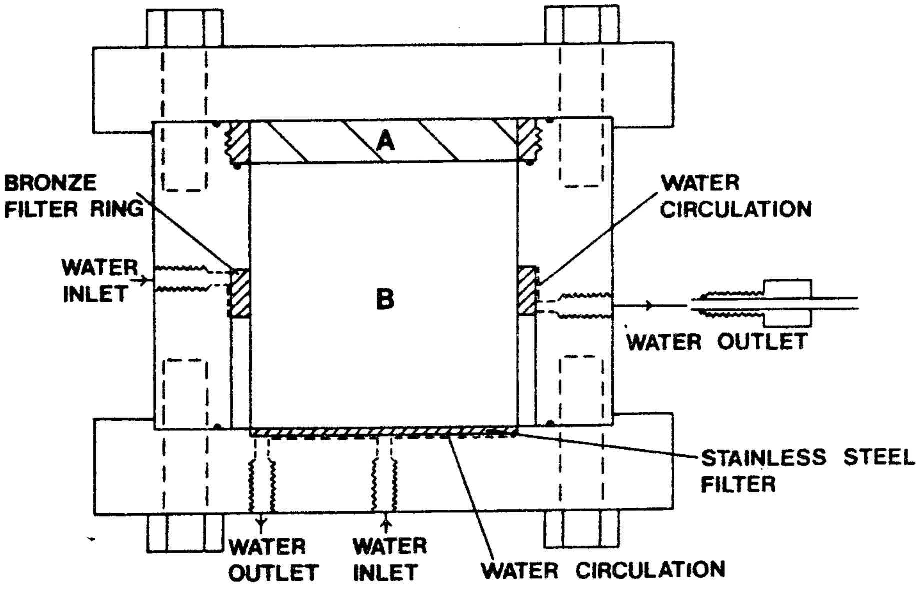


SEALING BODY USED IN WATERSATURATION BEFORE PUTTING A AND B TOGETHER



A ACTIVATED AND HOMOGENIZED BENTONITE
B HOMOGENIZED BENTONITE

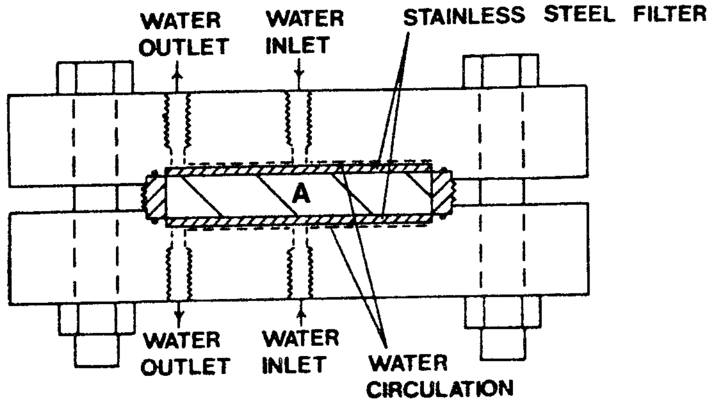


Figure 1.

The LuH swelling pressure oedometer. The compacted samples A and B were confined between filterstones through which water was passed during the saturation period. The radionuclides were added according to the methods described above.

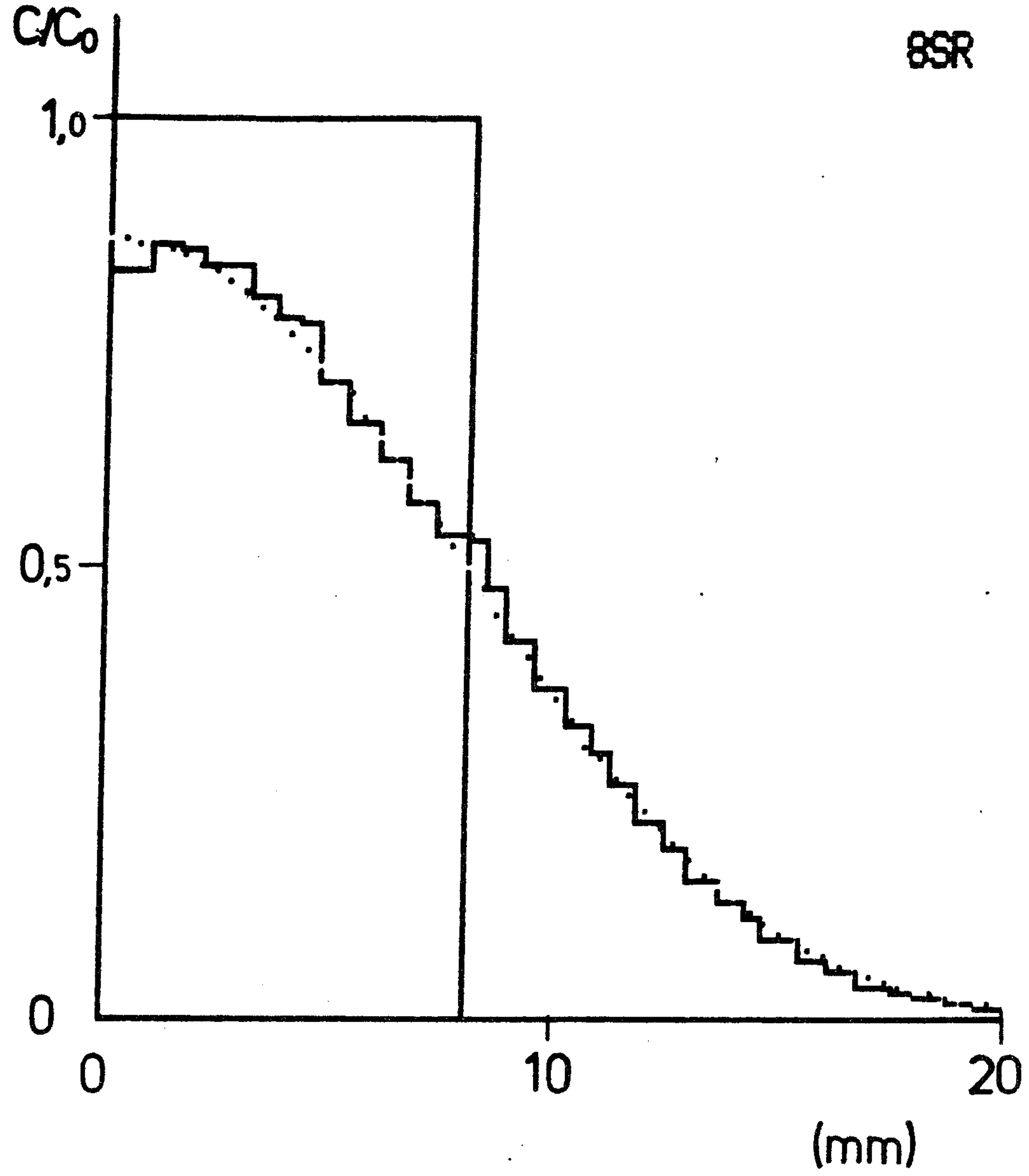


Figure 2.

^{85}Sr distributions in MX-80 bentonite (ρ = 2.1 ton$\cdot$m^{-3})
at t = 0 and t = 0.96$\cdot$10^{6} sec.
The dotted line describes the theoretical distribution with
D_p = 1.5$\cdot$10^{-11} m$^{2}\cdot$sec^{-1}.

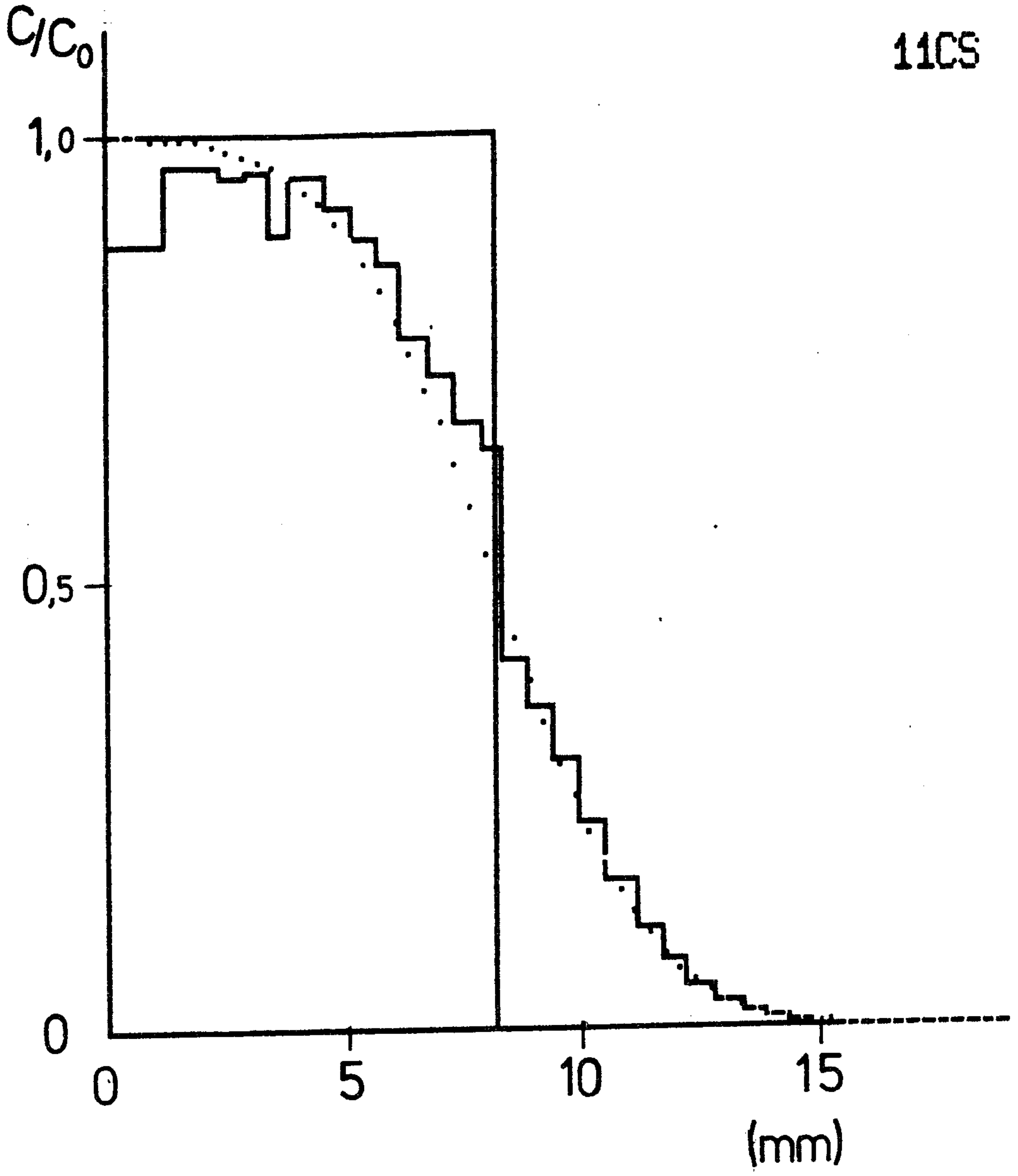


Figure 3.

^{134}Cs distributions in MX-80 (ρ = 2.1 ton·m^{-3}) at t = 0 and t = 1.72·10^6 sec.

The dotted line describes the theoretical distribution with D_p = 2·10^{-12} m^2·sec^{-1}.

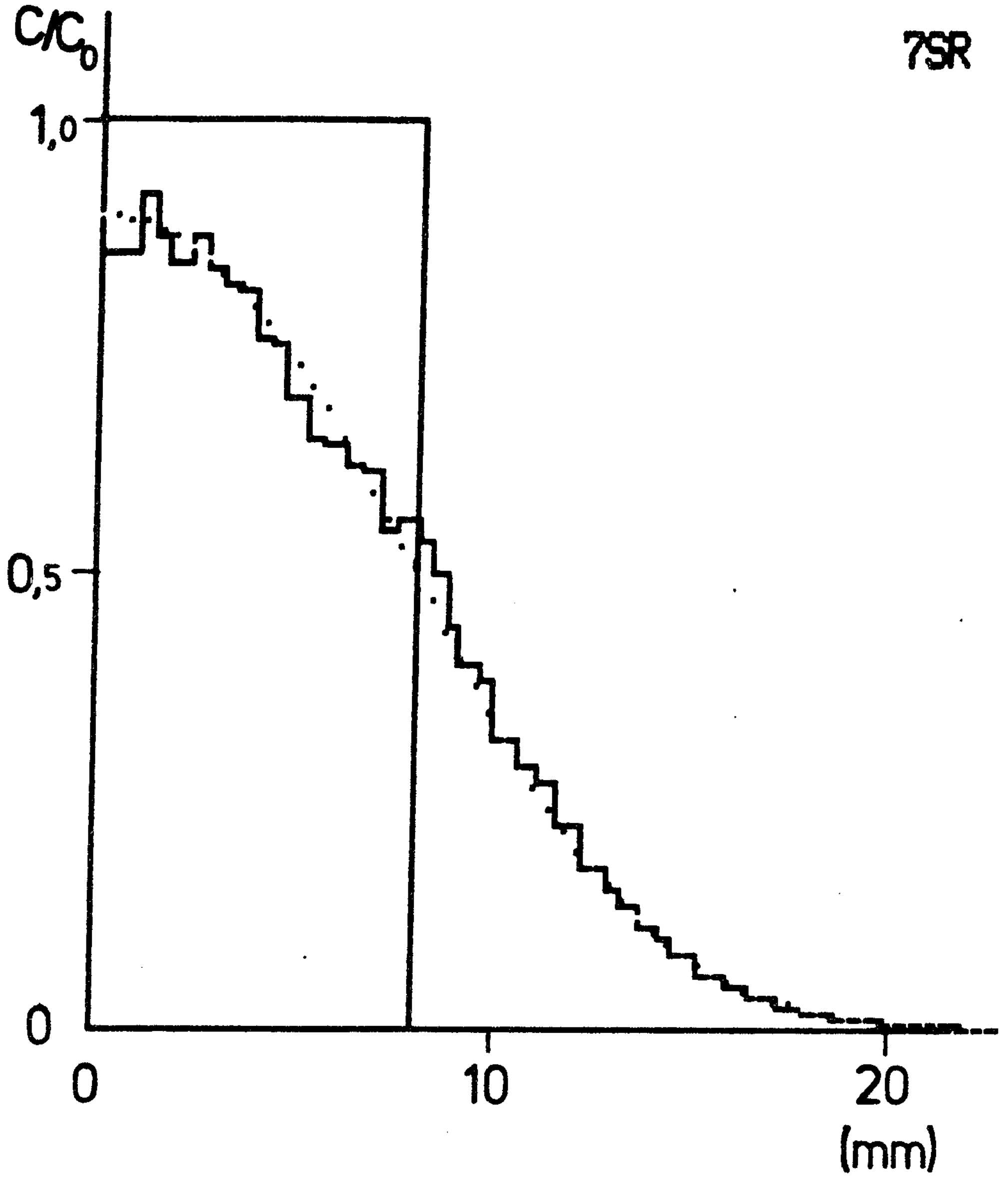


Figure 4.

^{85}Sr distributions in MX-80 bentonite (ρ = 2.1 ton·m^{-3})

at t = 0 and t = 0.92·10^6 sec.

The dotted line describes the theoretical distribution with

$D_p = 1.4 \cdot 10^{-11}$ m^2·sec^{-1}.

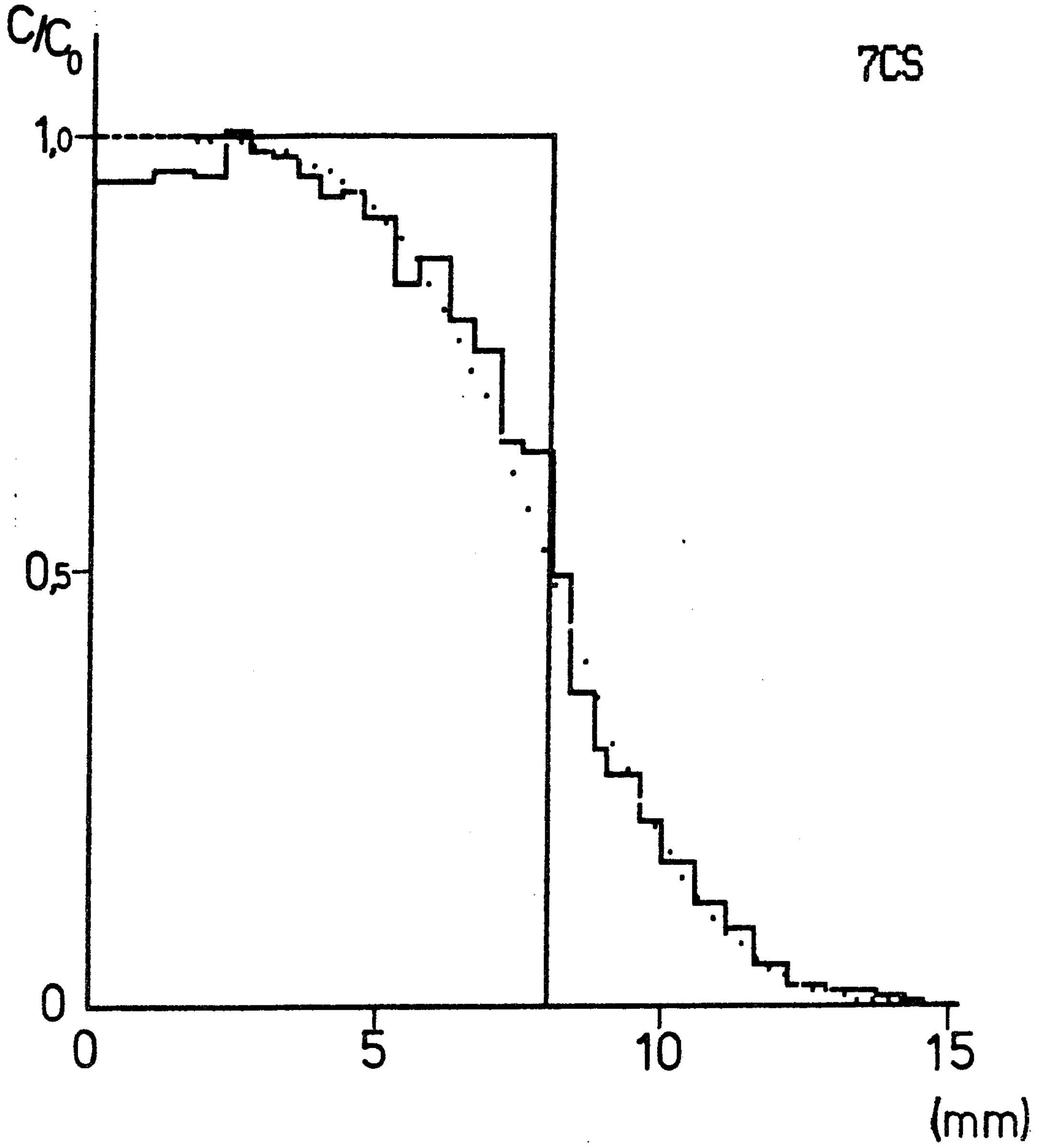


Figure 5.

^{134}Cs distributions in MX-80 (ρ = 2.1 ton·m^{-3}) at t = 0 and t = 0.864·10^{6} sec.

The dotted line describes the theoretical distribution with D_p = 3·10^{-12} m^{2}·sec^{-1}.

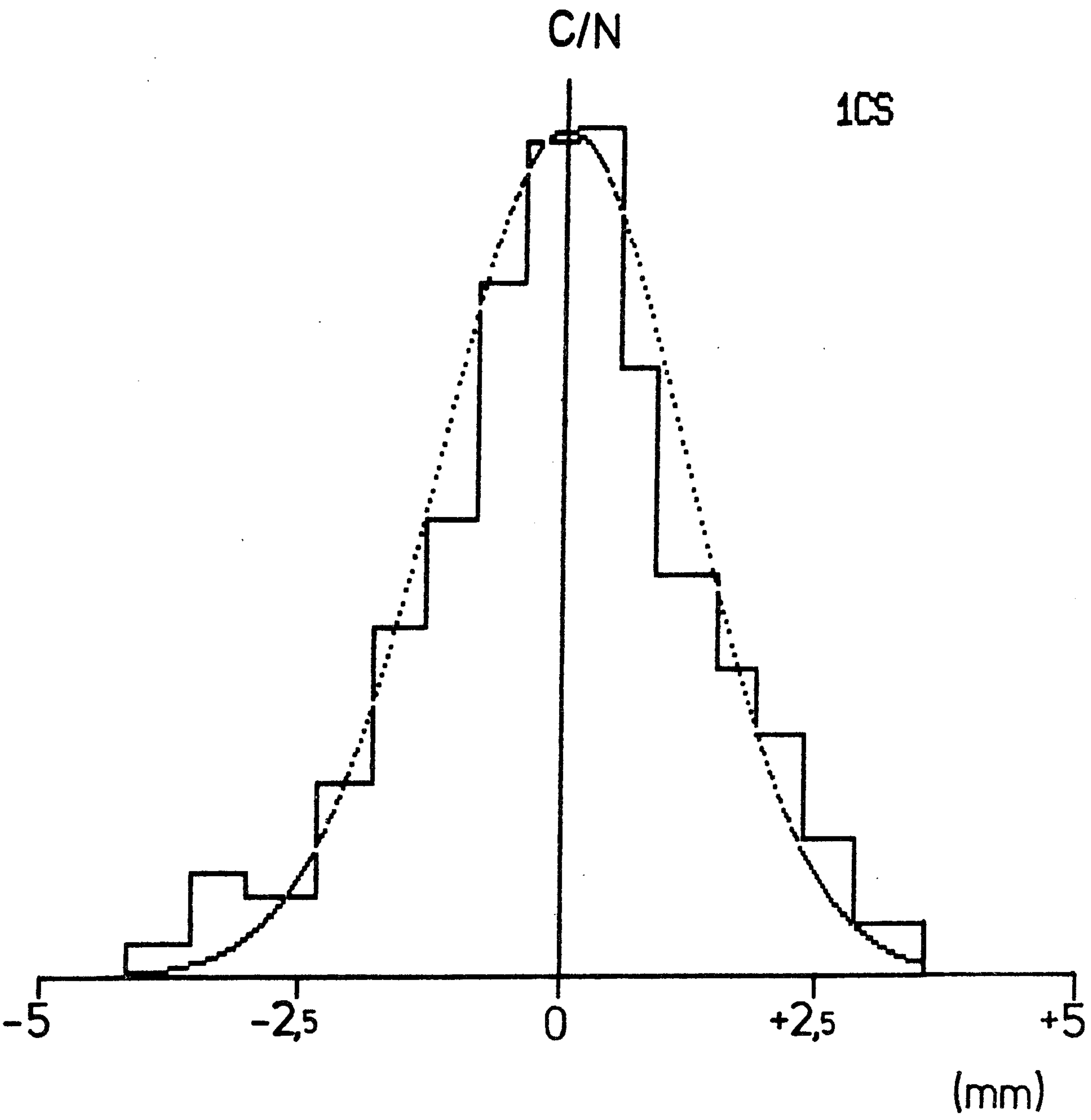


Figure 6.

^{134}Cs distribution in Erbslöh (ρ = 1.57 ton·m^{-3}) at t = 0.92·10^{6} sec. Dotted line gives theoretical distribution assuming instantaneous ^{134}Cs source and D_p = 7.5·10^{-13} m^{2}·sec^{-1}.

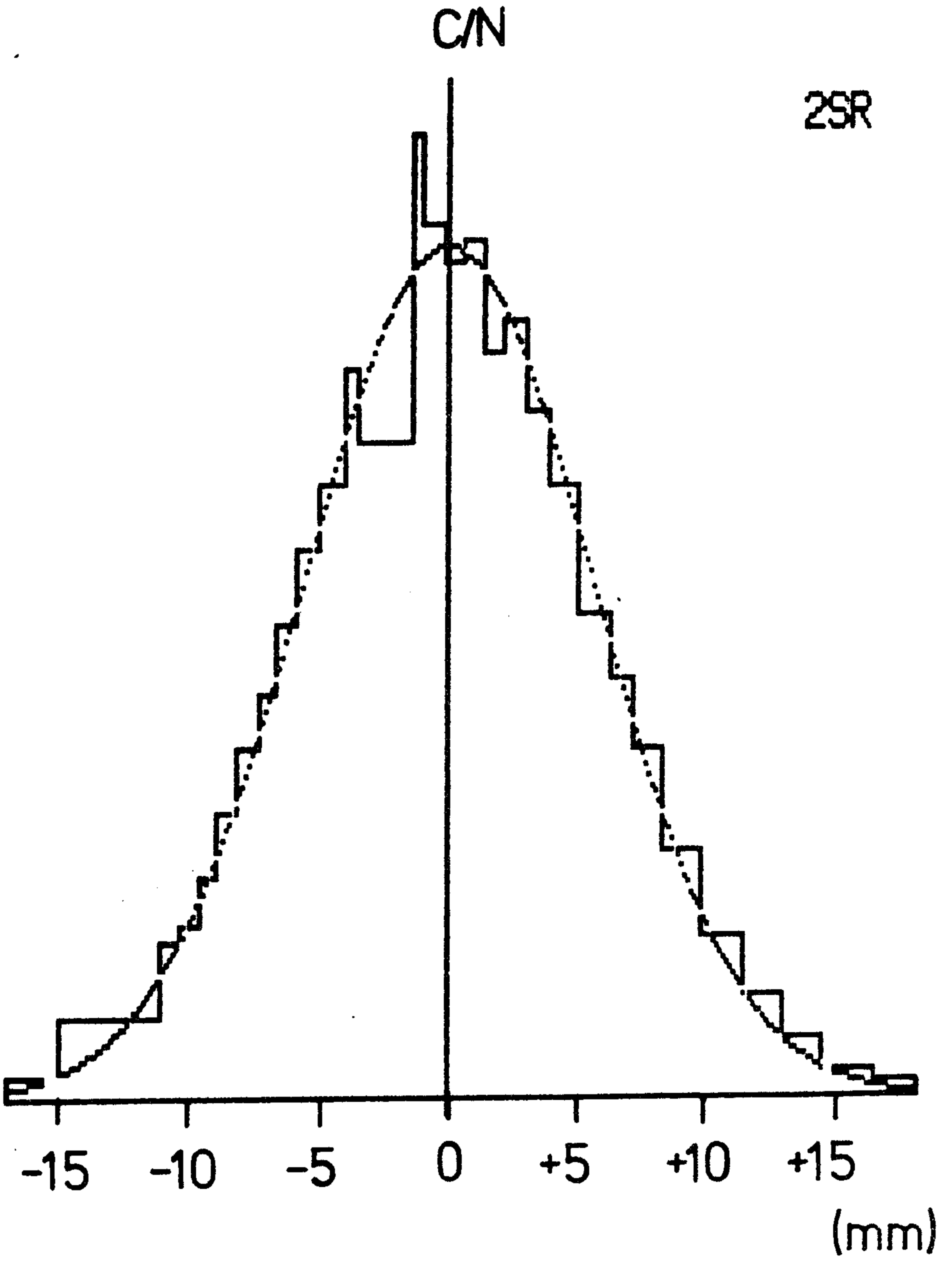


Figure 7.

^{85}Sr distribution in Erbslöh bentonite (ρ = 1.59 ton·m^{-3}) at t = 0.92·10^{6} sec.

Dotted line gives theoretical distribution assuming instantaneous ^{85}Sr source and D = 1.6·10^{-11} m^{2}·sec^{-1}.

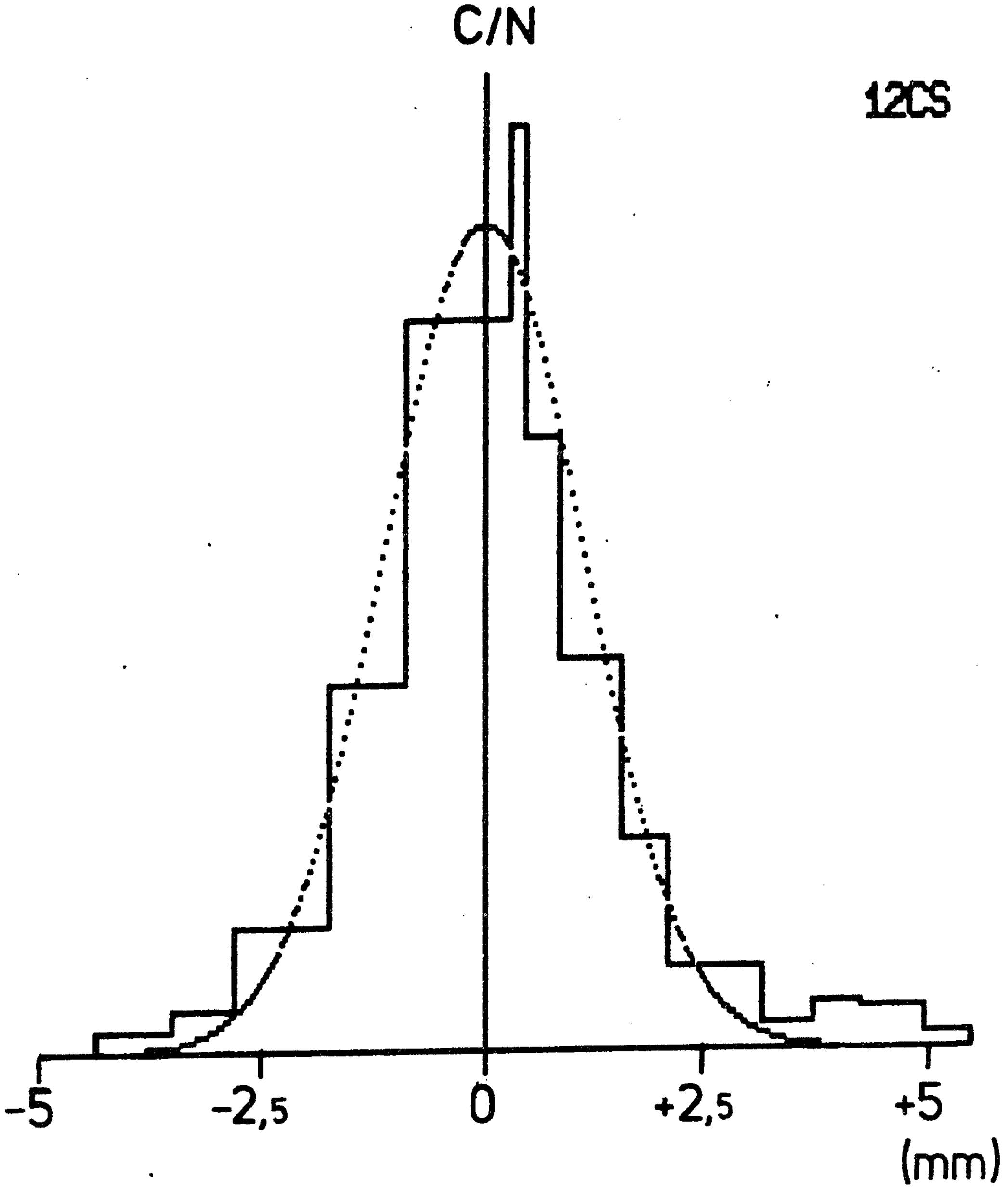


Figure 8.

^{134}Cs distribution in Erbslöh (ρ = 1.59 ton·m^{-3}) at t = 1.04·10^{6} sec.

Dotted line gives theoretical distribution assuming instantaneous ^{134}Cs source and D = 6·10^{-13} m^{2}·sec^{-1}.

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