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**Diffusion of hydrogen, hydrogen
sulfide and large molecular weight
anions in bentonite**

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MOLECULAR WEIGHT ANIONS IN BENTONITE

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A list of other reports published in this series during 1982, is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26) and 1981 (TR 81-17) is available through SKBF/KBS.

Diffusion of hydrogen, hydrogen sulfide and large molecular weight anions in bentonite.

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Summary

The diffusivities of HS^- and H_2 have been determined from profile analysis and steady state transport experiments.

The diffusivity of HS^- was found to be $9 \cdot 10^{-12}$ and $4 \cdot 10^{-12}$ $\text{m}^2 \cdot \text{sec}^{-1}$ in MX-80 and Erbslöh bentonite respectively. The results are in fair agreement with the results earlier obtained for Cl^- and I^- . The H_2 diffusivity calculated from steady state transport was found to be surprisingly low ($3.6 \cdot 10^{-12} \text{m}^2 \cdot \text{sec}^{-1}$). Various heavy anions with molecular weights $290-30 \cdot 10^3$ were found to migrate through MX-80 bentonite with diffusivities in the range $(2,1-0,75) \cdot 10^{-15} \text{m}^2 \cdot \text{sec}^{-1}$.

Handwritten notes:
 $7,5 \cdot 10^{-14}$ $9,4 \cdot 10^{-14}$
 $7,5 \cdot 10^{-14}$ $9,4 \cdot 10^{-14}$

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 saturated at its deposition and therefore will take up additional water from the rock. By swelling of the clay a perfect contact between the clay and rock might be created.

As the clay is assumed to create a first barrier for the transport of radionuclides from leaching canisters several diffusion studies have been carried out (1-6). From the corrosion point of view a knowledge of the diffusive transport of sulphide through the bentonite to the surfaces of the canisters as well as the outwards transport of hydrogen formed radiolytically near the canisters is important. A study of the diffusion of these species have therefore been carried out. The effect of ionic size on diffusive transport through the the clay has been the subject of a number of discussions and we have therefore in this study included a few anions with varying molecular weights.

Equipment and clay preparation

The experiments were carried out in swelling oedometers constructed at the University of Luleå (figure 1). Bentonite was compacted under nitrogen atmosphere (N_2) to desired density and thereafter contacted with water for 2-3 weeks. The experiments were carried out at 25°C in thermostated boxes.

Materials

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 was made with N_2 -

purged KBS-reference synthetic ground water "Allards" solution (KBS TR-report 98). The radionuclide ^{35}S was obtained as solid sodium sulphide (2-25 mCi/mmol) sealed under N_2 . Stock solution was prepared by dissolving the sodium sulphide in N_2 purged Allard water. The pKa values for H_2S and HS^- are 6.88 and 14.15 respectively (7) and the pH of the Allard solution is 8.8-8.9. Thus >90% of the tracer is present as H^{35}S^- . The hydrogen (H_2) used was of Aga SR-quality. Sodium anthraquinone-2-sulfonate (AQS $^-$, Fluka, pa), Disodium- 2,4,5,7 Tetrabromofluorescein (Eosin p.a. Merck) and Sodium-Lignosulfonate L5,6, L12 and L30 with anionic molecular weights 354, 646, 5600, 12000 and 30000 were used as received.

Experimental methods

HS^-

Two different techniques were used

I) H^{35}S^- solution (20 $\mu\text{Ci/ml}$) was equilibrated with a 8 mm thick bentonite disc in cell A (figure 1) for 3 weeks. The cells A and B were opened and thereafter mounted as shown in figure 1. By this procedure an extended source of limited extent was obtained. The oedometers were opened 17 days after onset of diffusion. Layers of known thickness were sliced off the bentonite cylinders and the radiation intensity of each of the serially surfaces measured using a GM detector with a thin end window (figure 2).

II) The diffusivities were also determined by adding a small volume of the tracer stock solution to solution on one side of the oedometer (21 $\mu\text{Ci/ml}$) and measuring the steady state transport of H^{35}S^- through a 8 mm thick bentonite disc. The ^{35}S concentration on both sides of the oedometer was measured by liquid scintillation counting.

H₂-diffusion

The diffusivity of H₂ was determined by measuring the transport through a 8 mm thick bentonite disc. The amount H₂ transported through the bentonite was measured gaschromatographically using a molecular sieve 13x column connected to a AGA-Argograf (figure 3).

Anion diffusion

The salts used were dissolved in the Allard solution on one side of the oedometer and the transport through 5 mm thick bentonite discs determined by spectrophotometric analysis of the solutions on both sides of the bentonite discs.

Evaluation of diffusion coefficients

- I) Profile analysis: the diffusion coefficients were calculated by fitting the experimental data to the following equation (8).

$$C(x,t) = C_0 \left(\operatorname{erf} \frac{1-x/h}{2/h \cdot \sqrt{Dt}} + \operatorname{erf} \frac{1+x/h}{2/h \cdot \sqrt{Dt}} \right) \quad (1)$$

where $C(x,t)$ = tracer concentration (radiation intensity) at distance x from surface

C_0 = initial tracer concentration in radionuclide containing volume

h = thickness of bentonite cylinder initially containing the radionuclide

t = time after onset of diffusion

D = diffusivity

II) The diffusion coefficient was calculated using the equation

$$V_2 \cdot \frac{dC_2}{dt} = A \cdot D \cdot \frac{(C_1 - C_2)}{x} \quad (2)$$

where A is the area of the bentonite in contact with the solutions

$C_1 - C_2$ concentration difference across the bentonite cylinder of thickness x

and V_2 volume of the low concentration solution.

It ought to be emphasized that the calculation is based on geometrical area and tracer concentration in solution.

Results

The distributions of ^{35}S within MX-80 and Erbslöh bentonites $1.5 \cdot 10^6$ sec after onset of diffusion are depicted in figures 4-5. The theoretical distributions according to equation (1) above are given by the dotted lines. In carrying out the calculations the measured radiation intensity of each of the serially exposed surfaces was assumed to represent the actual tracer concentration at the surface. This is not quite true, since the observed intensities contain contributions from layers beneath the surface. Several methods of calculating the true surface activity have been suggested (9) but we have not found it necessary to carry out any corrections for the following reasons. The β^- -energy of ^{35}S is 0.167 MeV which corresponds to a half-intensity distance of $3 \text{ mg} \cdot \text{cm}^{-2}$ i.e. 0.014 mm in the compacted clay. The counting efficiency falls off very sharply with the distance from the exposed surface as shown in figure 6. The change in ^{35}S concentration within 0.1 mm is only a few per cent, cf figures 4-5, and the relative contribution from inner layers to the measured radiation intensity of each of the serially exposed surfaces is thereby nearly constant.

The calculated diffusion coefficients are tabulated in table 1 together with the diffusion coefficients of HS^- and H_2 obtained in the steady state diffusion experiments (figures 7-8). For comparison diffusion coefficients for I^- and Cl^- obtained in an earlier study are included. In calculating the diffusion coefficient for H_2 the solubility of H_2 was taken to be $19.1 \text{ cm}^3 \cdot \text{dm}^{-3}$ (10). In measuring the optical absorption of the solution on the low concentration side of the bentonite disc a steady increase in absorption was observed over the whole wave length region 250-600 nm. Absorption spectra of the LS-30 solutions 45 days after onset of diffusion are shown in figure 9. The absorbance of AQS^- and LS-30 on the low concentration of the bentonite are plotted in vs time in figure 10. The diffusivities calculated from these plots are given in table 2 together with the lower limits estimated from short time experiment.

Discussion

The diffusivities for HS^- calculated from profile analysis are nearly the same as earlier obtained for Cl^- ions. The diffusivity is about a factor two lower in Erbslöh as compared to MX-80. The diffusivity of HS^- in MX-80 obtained from steady state diffusion is, however, one order of magnitude lower than the Cl^- diffusivity obtained in similar experiments. On equilibrating the MX-80 and Erbslöh bentonites with H^{35}S^- solution we observed that the radiation intensity of the MX-80 surface after equilibration was only ~ 20% of the radiation intensity of the Erbslöh surface. The sulphur content of the two bentonites studied have been found to be (11)

MX-80	(0.23% total, 0.11-0.13% as sulfides)
Erbslöh	~ 0.01%.

One difficulty in correlating the diffusivities obtained from profile analysis to the diffusivities calculated from steady state tran-

sport data is the lack of knowledge of the tracer concentration at the solution-bentonite interface. This concentration is generally higher for sorbing species like positive ions (counterions to the bentonite) and lower for negative ions (coions to the bentonite) as shown schematically in figure 11. The equilibrium concentration of any ion in the bentonite and solution respectively is a function of the ionic charge, the ionic strength of the solution and the overall exchanger composition and thereby not readily calculated. The difference in $H^{35}S^-$ concentration in the two bentonites probably at least partly reflects the difference in sulfide content of the two bentonites.

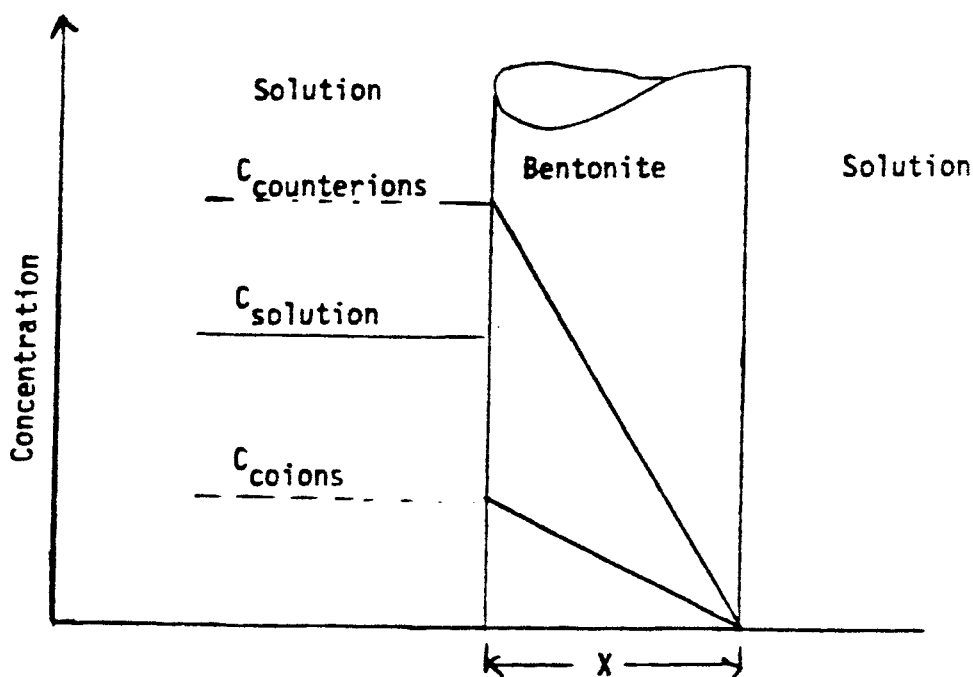


Fig. 11

The H_2 diffusivity measured in this study is about a factor five lower than the diffusivity obtained by Neretnieks (2) in a similar experiment. This difference may possibly be due to experimental differences in filterstones and bentonite densities. In both studies the H_2 diffusivity obtained is surprisingly low and may indicate some adsorption of H_2 on the bentonite.

Table 1.

Diffusivities at 25°C for HS⁻, Cl⁻, I⁻ and H₂ calculated from concentration profile analysis (a) and steady state transport (b).

Bentonite	Density ton·m ⁻³	D _{obs} × 10 ¹³ m ² ·sec ⁻¹				Method
		Cl ⁻	I ⁻	HS ⁻	H ₂	
MX-80	2.1	60	40	90	-	(a)
		3.1	2.1	0.18	36	(b)
Erbslöh	2.1		10	40		(a)
			1.3			(b)

Table 2.

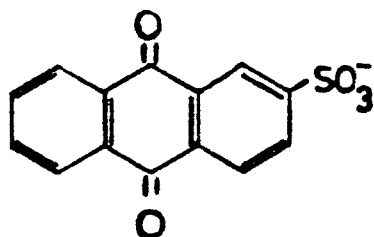
Diffusivities in MX-80 (= 2.1 ton·m⁻³) of various anions, calculated from steady state transport.

Anions	Molwt	D _{obs} · 10 ¹⁵ m ² ·sec ⁻¹	
AQS ⁻	290	> 2 ^{a)}	2.10 ^{b)}
Eosin	548	> 0.6	
LS 5,6	5.6 · 10 ³	> 1.0	
LS 12	12 · 10 ³	> 0.5	
LS 30	30 · 10 ³	> 0.1	0.75

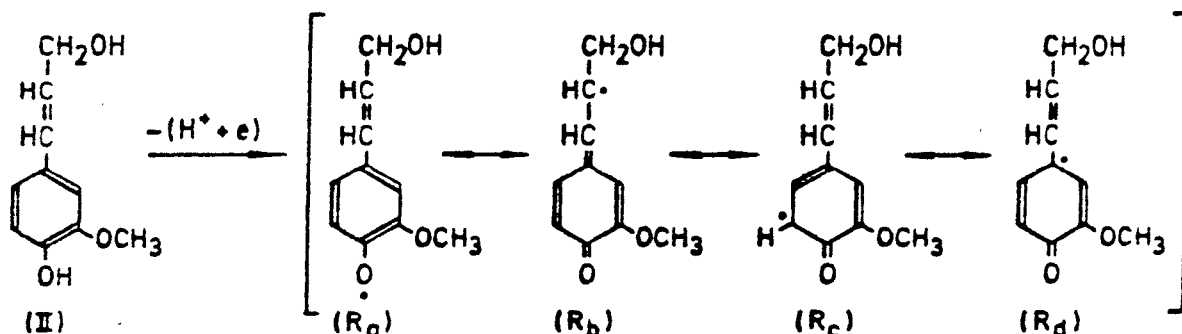
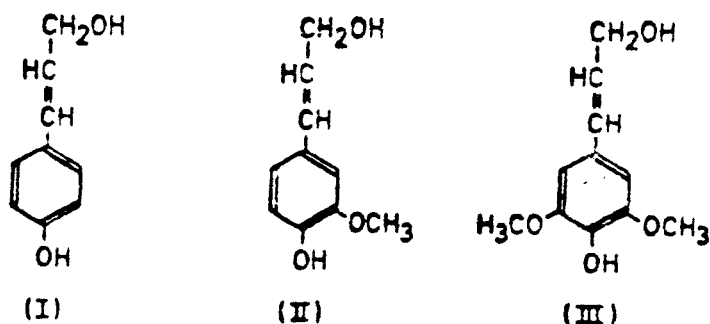
a) estimated from short time experiment.

b) calculated from data plotted in fig. 10.

The diffusivities of AQS^- and LS-30 are surprisingly high. The molecular structure of AQS^- is planar and the size about $5 \times 8 \text{ \AA}$.



The structure and size of LS-30 are not known, but a rough estimate can be given based on the following assumptions. Lignin is a natural polymeric product arising from dehydrogenative polymerization of the p-coumaryl (I), coniferyl (II) and sinapyl (III) alcohols. Since the polymerization is a radical process involving a number of resonant radical forms (R_a - R_d)



LS-30 most probably has a spherical structure. From the alcoholic structures and molweights the LS-30 ion may be considered to consist of 150-180 units with diameter ~ 8 Å. Assuming spherical structure the diameter of the LS-30 ion is estimated to be about (40-45) Å. A comparison of the diffusivities of the anions studied gives no indication of "pore filtering" effect on the diffusivity.

Acknowledgements

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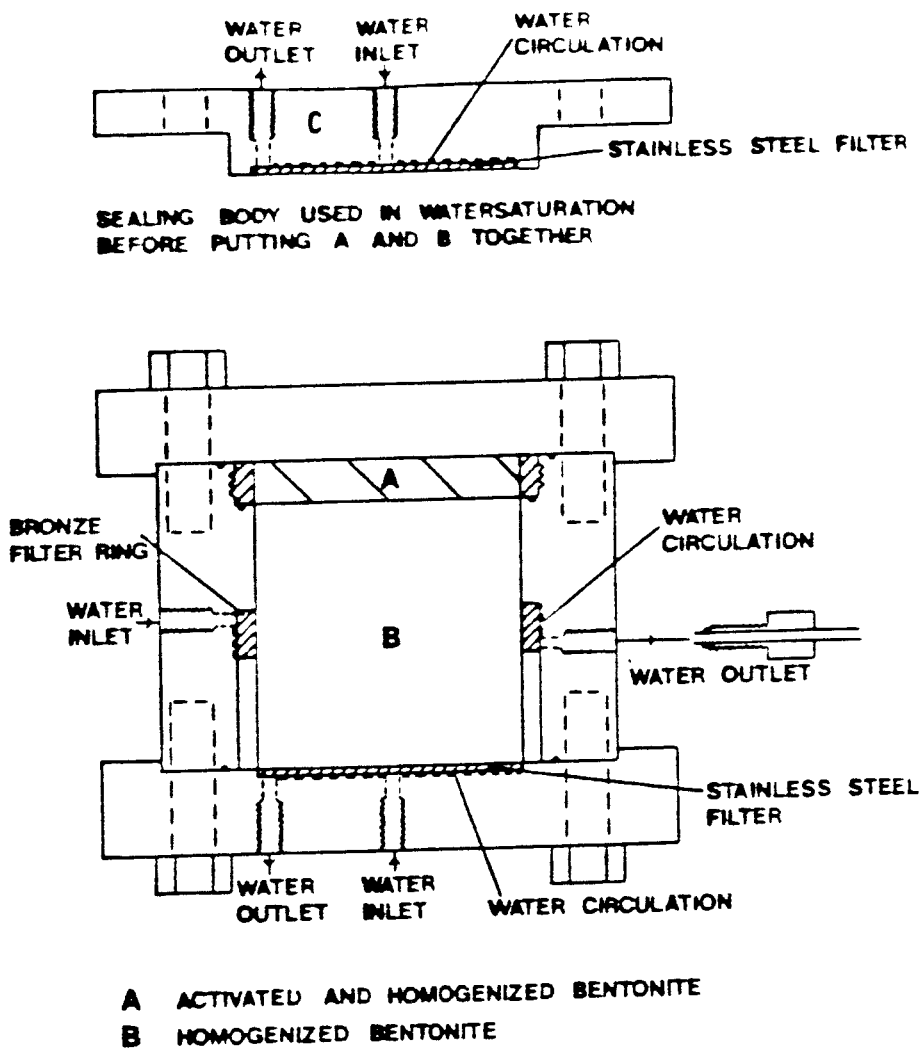


Figure 1.

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.

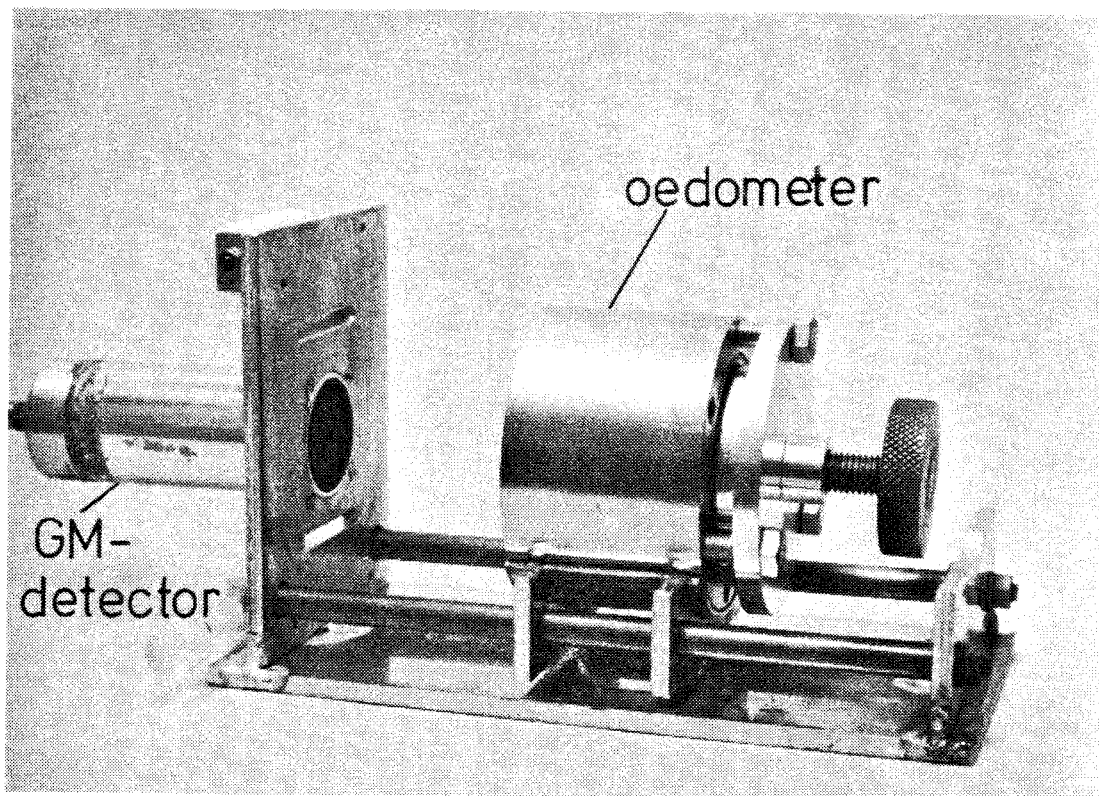


Figure 2.
Experimental equipment for measurement of the radiation
intensity of the serially exposed bentonite surfaces.

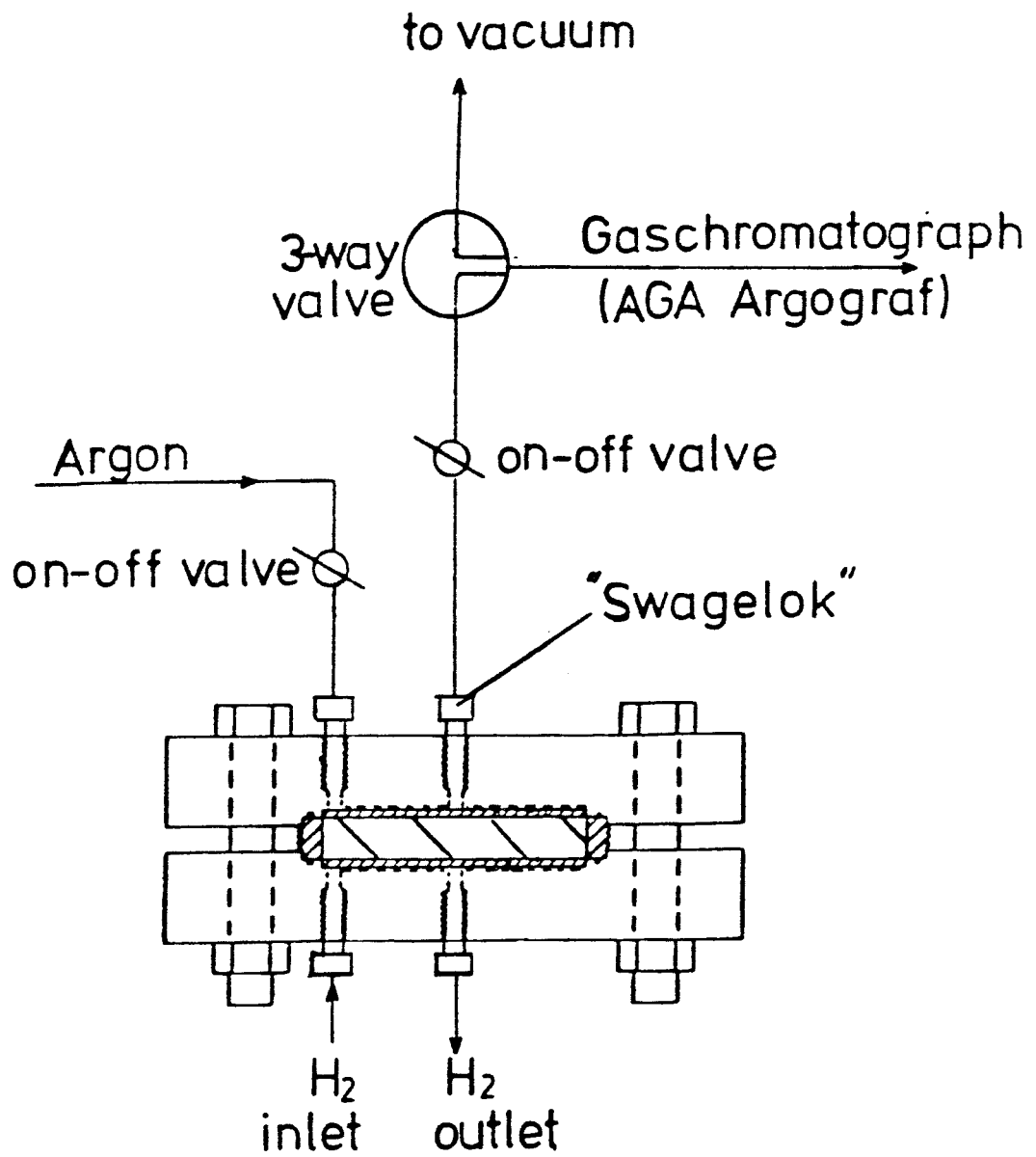


Figure 3.

Schematic drawing of equipment used for measuring hydrogen (H₂) diffusion.

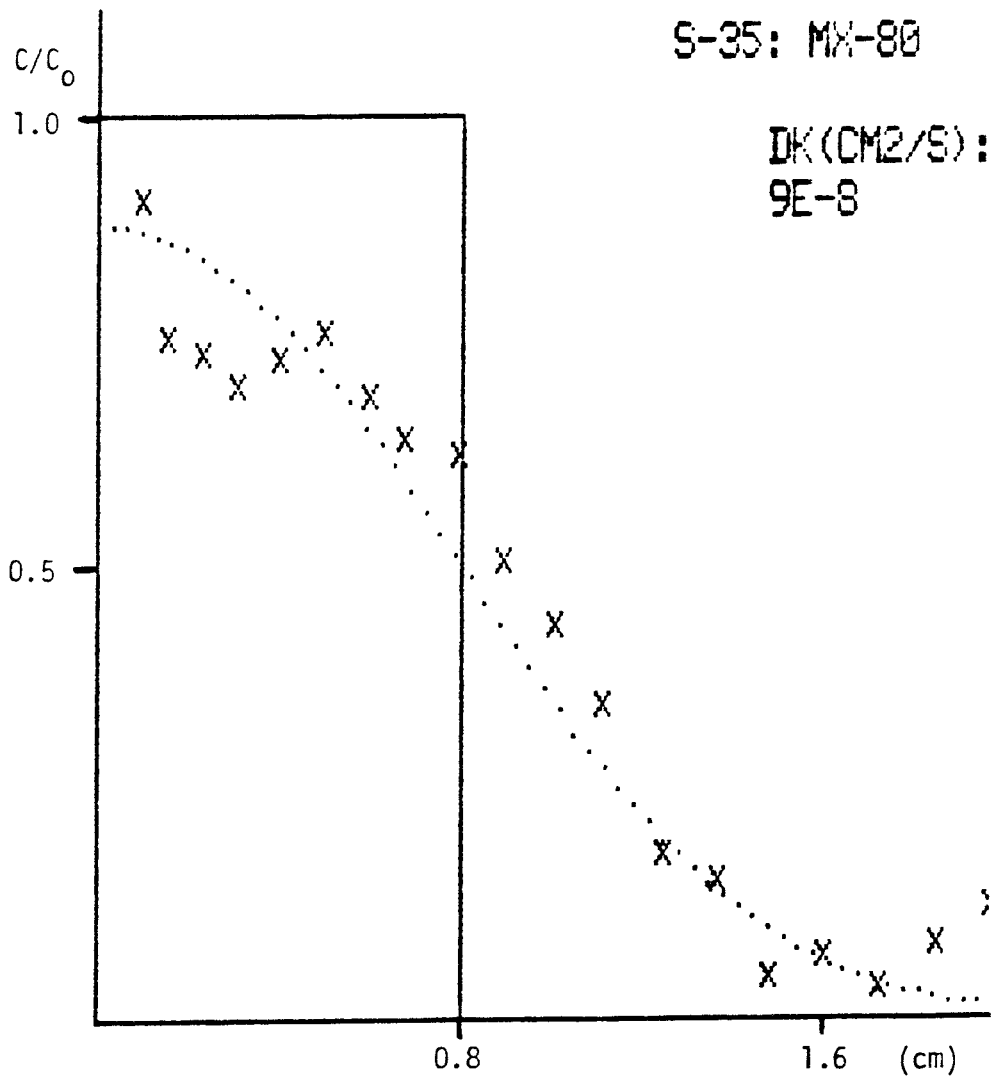


Figure 4.

³⁵S distribution in MX-80 ($\rho = 2.1 \text{ ton}\cdot\text{m}^{-3}$) at $t = 1.48 \cdot 10^6 \text{ sec}$.
 The dotted line describes the theoretical distribution assuming
 $D_{\text{obs}} = 9 \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$.

The solid line represents the initial stage.

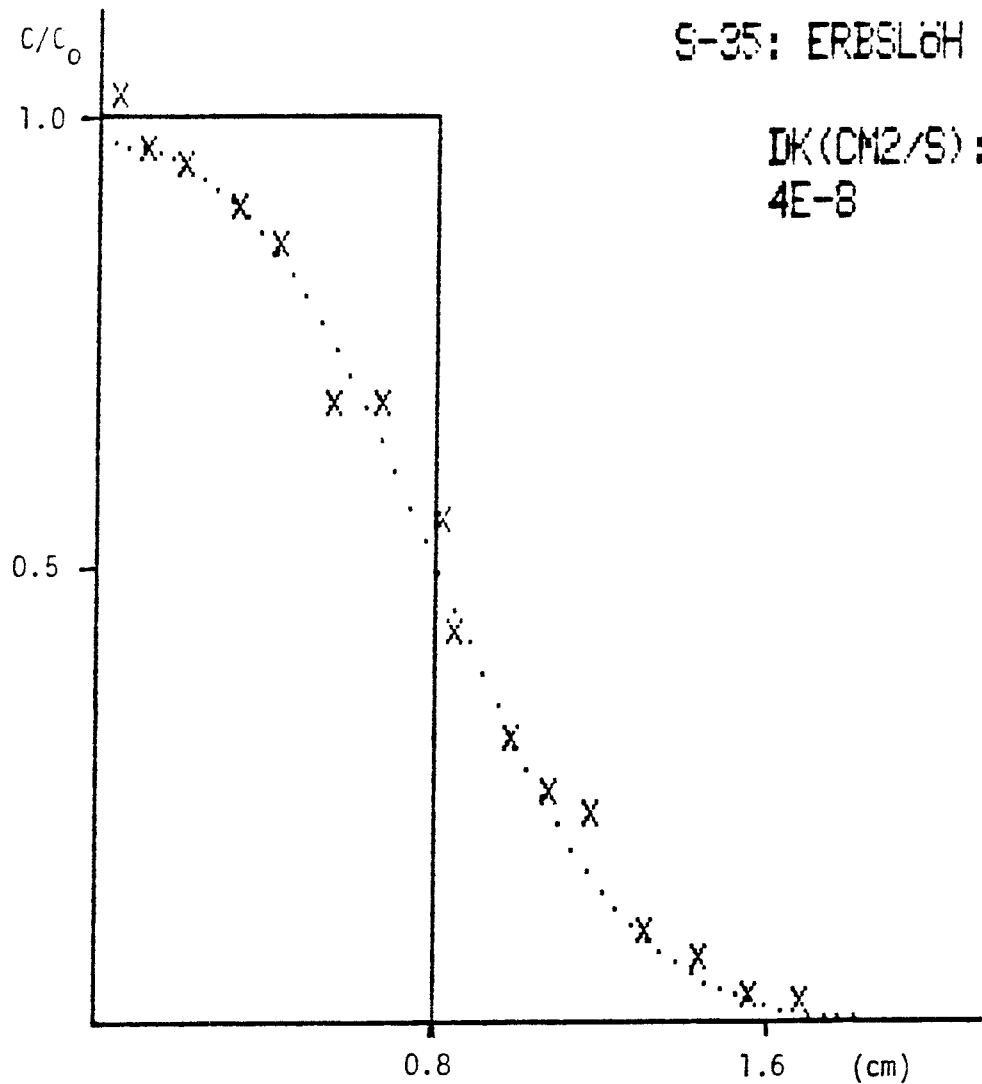


Figure 5.

³⁵S distribution in Erbslöh bentonite ($\rho = 2.1 \text{ ton}\cdot\text{m}^{-3}$) at
 $t = 1.5 \cdot 10^6 \text{ sec}$.

The dotted line describes the theoretical distribution assuming
 $D_{\text{obs}} = 4 \cdot 10^{-12} \text{ m}^2 \cdot \text{sec}^{-1}$.

The solid line represents the initial stage.

Figure 6.

Relative detection efficiency at surface of bentonite with density $2.1 \text{ ton}\cdot\text{m}^{-3}$ as function of ^{35}S -source distance from surface, assuming constant detecting geometry.

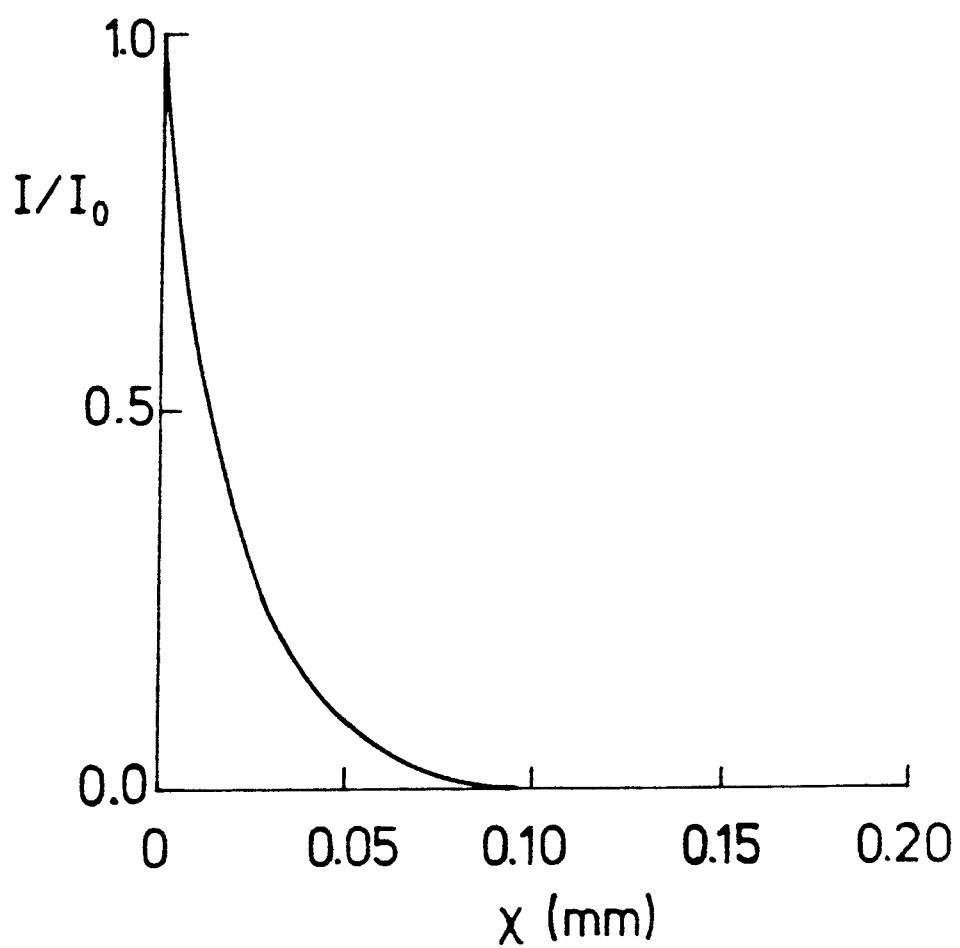


Figure 7.

Accumulated ^{35}S in solution on low activity side of bentonite
($x = 0.5 \text{ cm}$, $A = 19.63 \text{ cm}^2$)

^{35}S concentration in solution on high activity side of bentonite

- left hand scale
- △ right hand scale

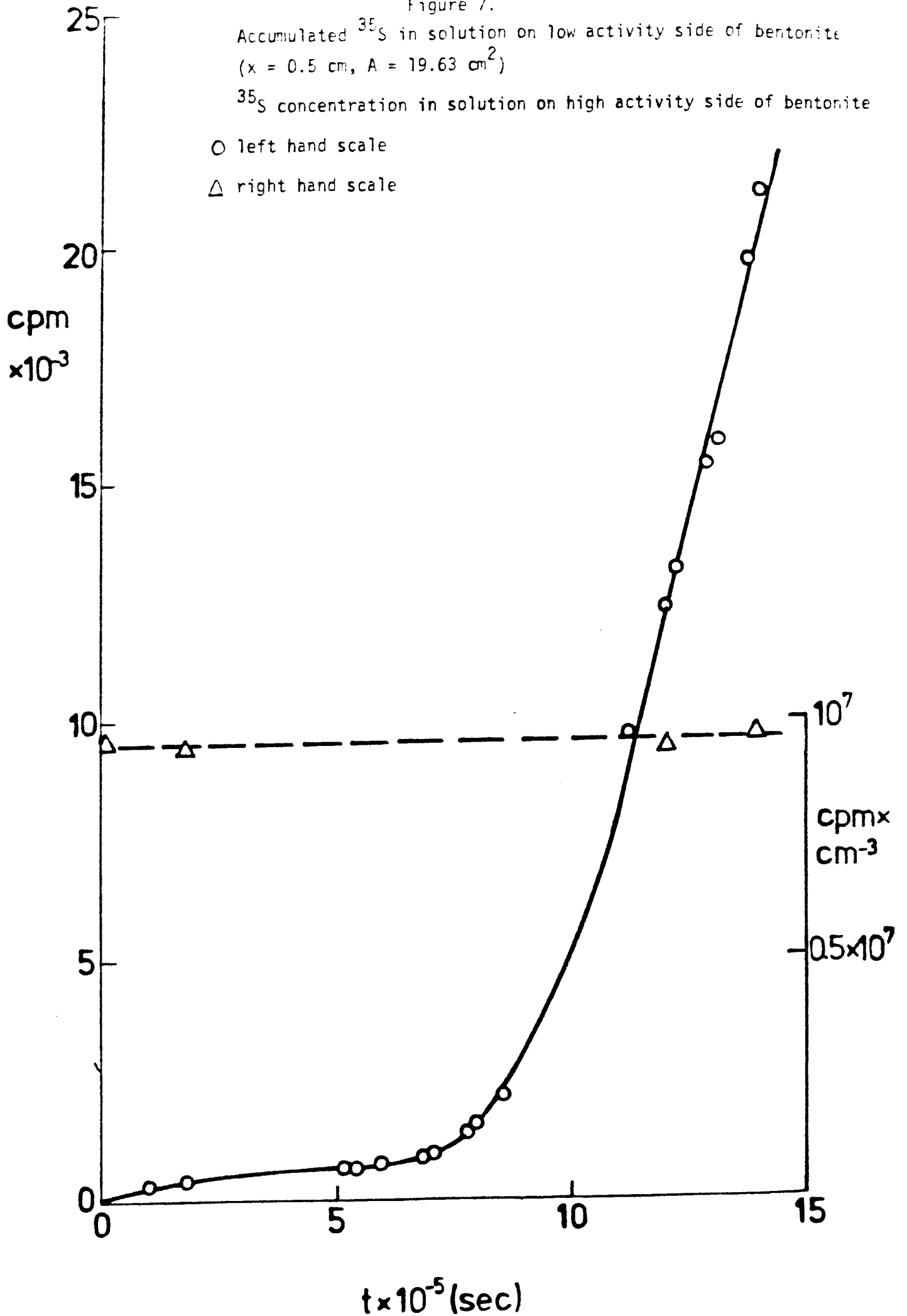
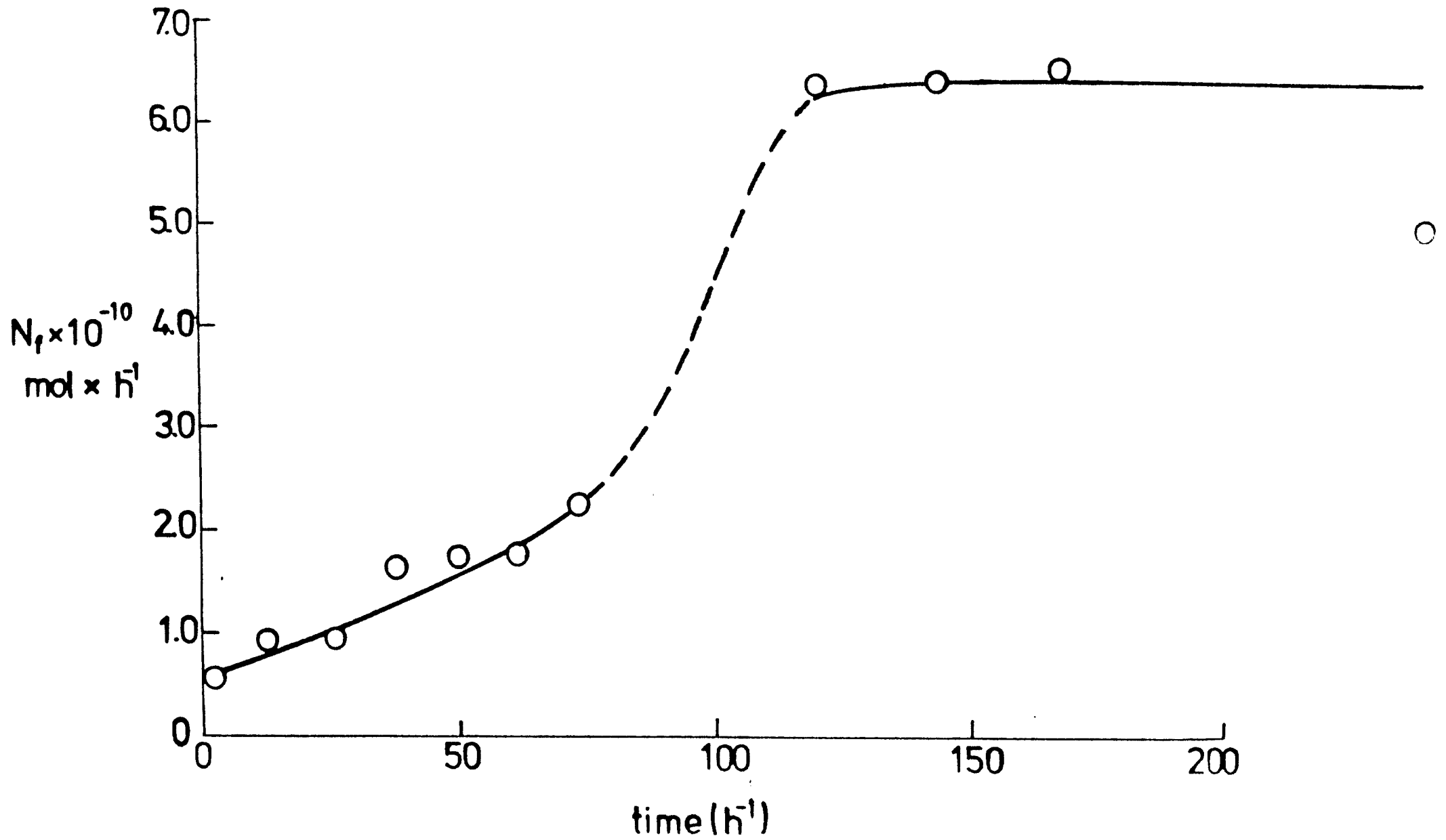


Figure 8.

Hydrogen transport through MX-80 bentonite ($\rho = 2.1 \text{ ton}\cdot\text{m}^{-3}$) as function of time ($A = 19.63 \text{ cm}^2$,
 $x = 0.8 \text{ cm}$)



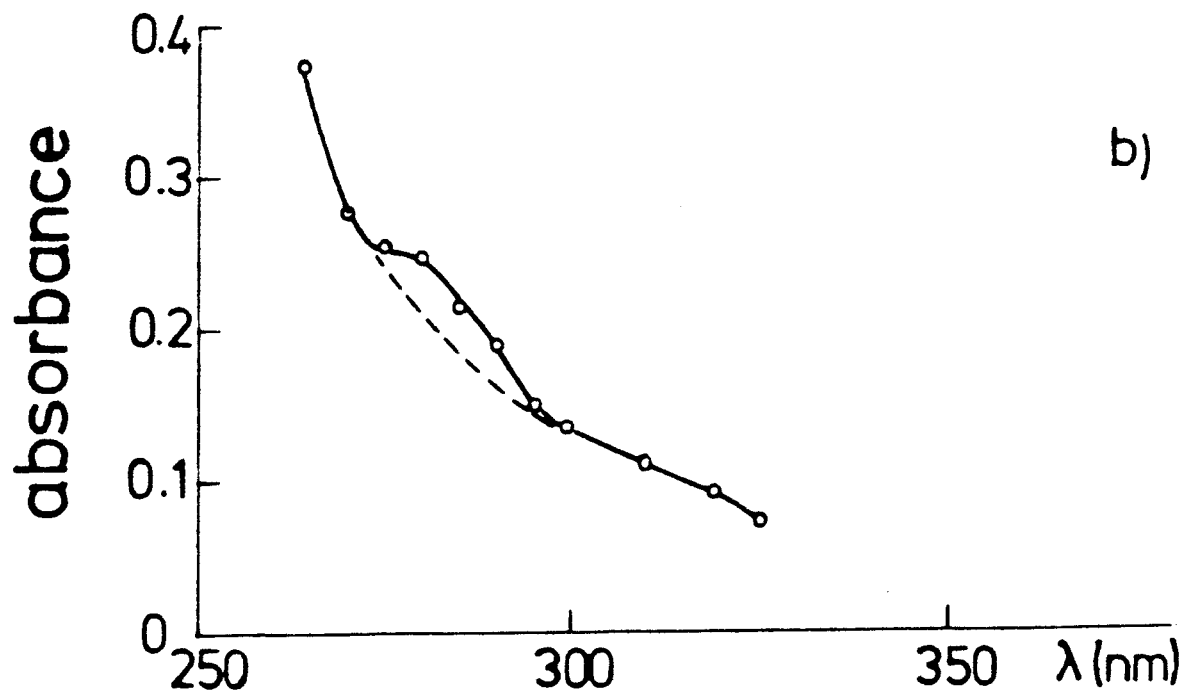
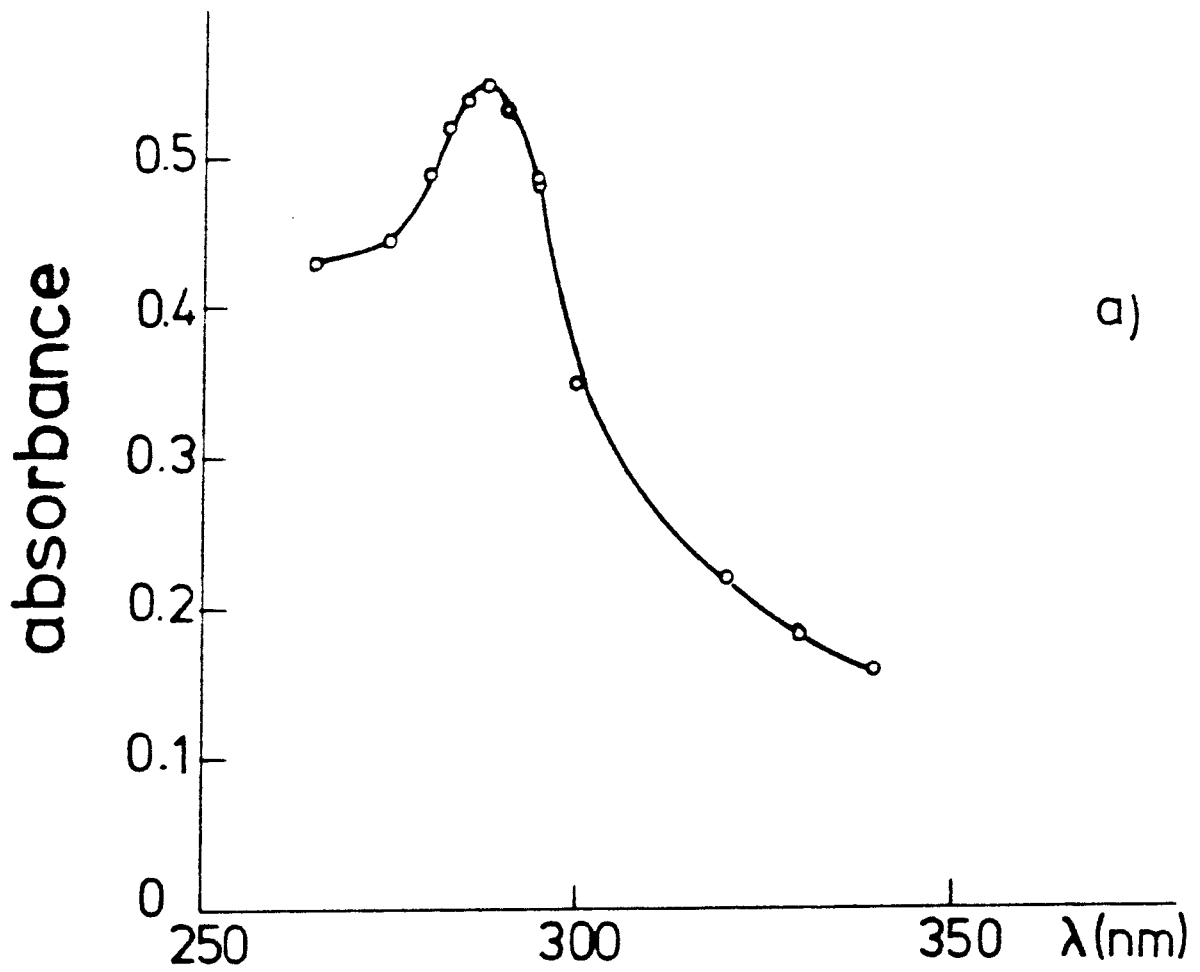


Figure 9.

- a) Absorption spectrum of LS-30 reference solution ($2 \cdot 10^{-3} \text{ cm}^3$ diluted to 1 cm^3)
- b) Absorption spectrum of solution on low concentration side of bentonite ($A = 19.63 \text{ cm}^2$, $x = 0.5 \text{ cm}$, $t = 45 \text{ days}$, 1 cm optical path length)

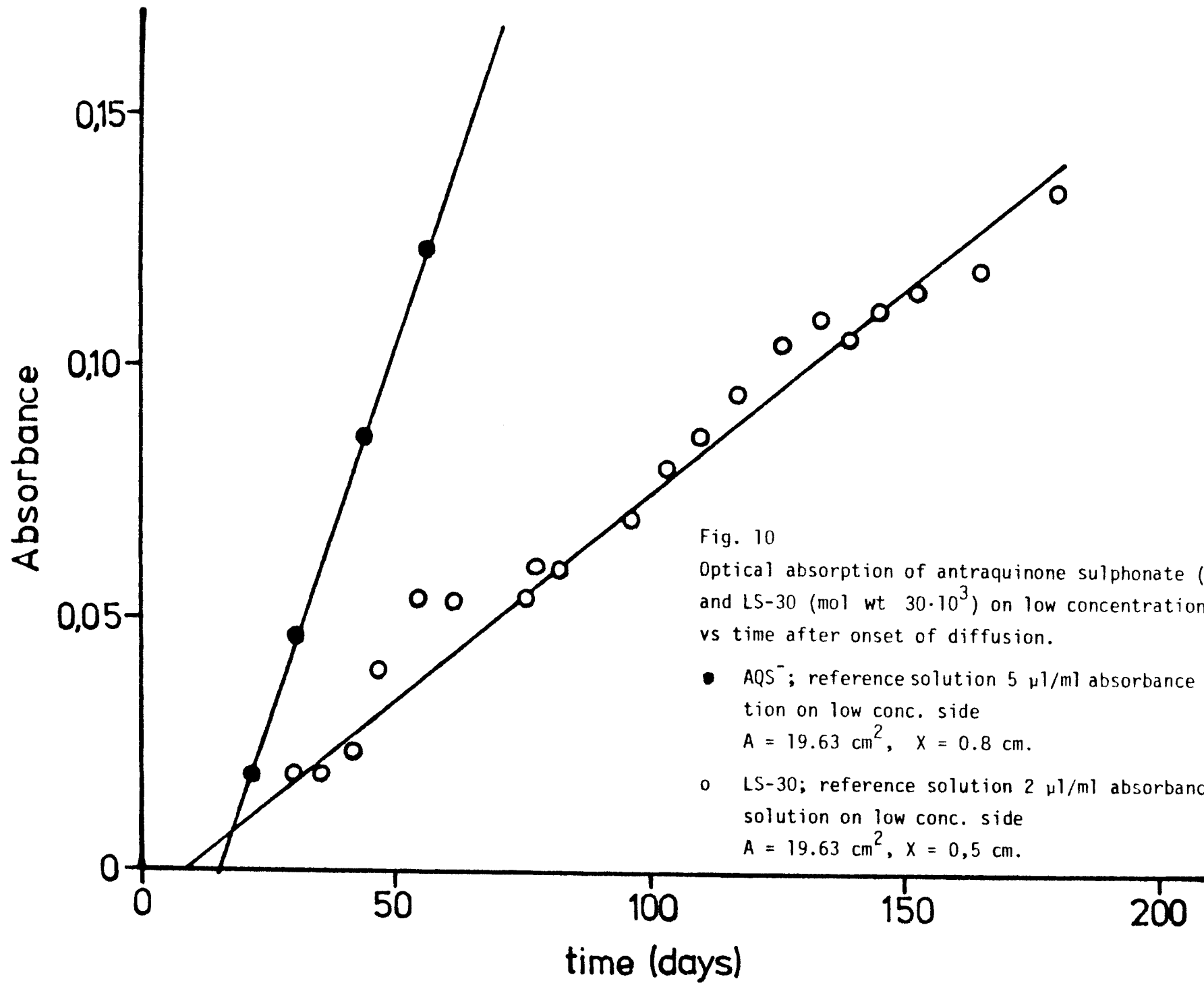


Fig. 10
Optical absorption of antraquinone sulphonate (mol wt. 290) and LS-30 (mol wt $30 \cdot 10^3$) on low concentration side of bentonite vs time after onset of diffusion.

- AQS⁻; reference solution 5 $\mu\text{l/ml}$ absorbance 0,35, 3 ml solution on low conc. side
 $A = 19.63 \text{ cm}^2$, $X = 0.8 \text{ cm}$.
- LS-30; reference solution 2 $\mu\text{l/ml}$ absorbance 0,18, 3 ml solution on low conc. side
 $A = 19.63 \text{ cm}^2$, $X = 0,5 \text{ cm}$.

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