

**Radiolysis of ground water: influence of
carbonate and chloride on the hydrogen
peroxide production**

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RADIOLYSIS OF GROUND WATER: INFLUENCE OF CARBONATE
AND CHLORIDE ON THE HYDROGEN PEROXIDE PRODUCTION

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Abstract

Small volumes of aqueous solutions have been subjected to α -radiation from a Am-241 source. The irradiated solution was separated from the bulk solution by a glass filter serving as a diffusion barrier.

The H_2O_2 concentration in the bulk solution was monitored by a chemiluminescence technique and the overall production of oxidizing species ($\text{H}_2\text{O}_2/\text{O}_2$) in irradiated ground water was studied by measuring the Fe^{2+} -consumption in ground water initially containing $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \text{ Fe}^{2+}$.

H_2O_2 yields calculated using the computer program CHEMSIMUL are in fair agreement with experimental yields for "pure" water (pH 8) and aqueous methanol solutions (pH 5).

Experimentally $G(\text{H}_2\text{O}_2) = 1.06 \pm 0.1$ was obtained in "pure" water. In solutions containing $2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ HCO}_3^-$ and in ground water $G(\text{H}_2\text{O}_2)$ decreased to 0.69 ± 0.03 . A corresponding decrease in $G(\text{H}_2\text{O}_2)$ was not found in the calculations. The agreement between measured and calculated Fe^{2+} consumption is fair when slow oxidative reactions in the bulk solutions are taken into account.

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1. INTRODUCTION

The effect of radiation on water carrying geological material e.g. bentonite backfill may be due to direct radiation damage and changes in the water chemistry due to water radiolysis. The yields (i.e. G-values) of the primary products $\cdot\text{OH}$, e^-_{aq} , $\text{H}\cdot$, H_2O_2 , H_2 , $\text{HO}_2\cdot$, H_3O^+ formed by radiolysis of water are strongly dependent on the LET (Linear Energy Transfer) of the radiation. In a closed system irradiated with low LET radiation e.g. gamma, the radical products $\cdot\text{OH}$, e^-_{aq} , $\text{H}\cdot$ being formed in higher yields than the molecular products H_2O_2 and H_2 react with the latter in such a way that no net decomposition of the water occurs (Allen 1961). For high LET radiation the molecular yields are higher than the radical yields resulting in net decomposition of water.

In an open system e.g. a water saturated bentonite reactions between radiolytic products and dissolved species in the pore water as well as diffusion out of the irradiated volume may strongly influence the chemical effects of the radiolysis. Due to its high diffusivity and low reactivity molecular hydrogen (H_2) may diffuse out of the irradiated volume. The oxidizing products are more reactive and may thereby create a moving redox front (Neretnieks 1982; Neretnieks and Åslund 1983).

The diffusion of H_2 out of β^- , γ , and α -irradiated water-saturated compacted bentonite have been subjected to several experimental and modelling studies (Eriksen and Jacobsson 1983; Eriksen et al 1987). The present report deals with the

radiolytic production on hydrogen peroxide (H_2O_2) in aqueous solutions containing HCO_3^- , Cl^- and Fe^{2+} .

2. EXPERIMENTAL

2.1 Radiation source

The radiation source consisted of Am-241 incorporated in a gold matrix on silver backing. The α -emitting surface was covered by a 2 μm thick gold-palladium alloy. The diameter of the active surface was 25 mm and the total activity 35.7 MBq. The average energy of the α -particles leaving the surface was determined (Eriksen et al; 1987) by α -spectroscopy to be 4.6 MeV and the energy deposition $8.22 \cdot 10^{13} \text{ eV} \cdot \text{s}^{-1}$. Assuming the range of the α -particles to be 37 μm in water (Flügge 1958) the volume of the irradiated solution was $1.81 \cdot 10^{-2} \text{ cm}^3$ and the average dose rate 73 rad s^{-1} .

2.2 Experimental set up

The experimental arrangement is shown schematically in Fig. 1. A glass filter ($d = 65 \text{ mm}$) was placed close to the α -emitting surface (distance approximately 0,2 mm) of the radiation source to secure diffusive transport of radiolytic products out of the irradiated volume. The radiolytic products H_2 , O_2 and H_2O_2 thus diffused out of irradiated volume into the inner aqueous phase and subsequently through the glass filter into the outer aqueous phase. The volume of the outer aqueous phase

was 110 cm³. All chemical analyses were carried out on samples taken from this volume.

2.3 Irradiated solutions

All chemicals (p.a. quality) were used as received. Solutions were prepared from deionized water double distilled in quartz apparatus and freed from oxygen by purging with Ar (AGA-SR-quality) containing less than 1 ppm O₂.

The following solutions were irradiated;

1a: aq. dest, K₂HPO₄ buffer, pH = 8

1b: 2·10⁻³ mol·dm⁻³ HCO₃⁻, pH = 8

1c: Synthetic ground water^x), pH = 8-8.2

1d: Synthetic ground water^x), 2·10⁻⁶ mol·dm⁻³ Fe²⁺,
pH = 8-8.2

2: 0.5 mol·dm⁻³ MeOH, pH = 5, (dosimeter solution)

x) Principal ions, 123 ppm HCO₃⁻, 70 ppm Cl⁻,
65 ppm K⁺, see Table 1.

2.4 Analysis

The hydrogen peroxide (H₂O₂) production in the irradiated solutions 1a, 1b, 1c and 2 was monitored using a chemiluminescence method. 100 µl solution was added to 2 ml reagent containing 2·10⁻⁵ mol·dm⁻³ luminol (5-amino-2,3 dihydro-1,4 phtalazinedione) and 2·10⁻⁵ mol·dm⁻³ Cu²⁺ and the light emission was measured with a LKB-1250 luminometer. The

Fe^{2+} consumption by oxidants formed on irradiation of solution was determined colorimetrically with o-phenanthroline (Gerstl and Banin 1980; Fortune and Mellon 1938).

3. EXPERIMENTAL RESULTS

3.1 Diffusion

The diffusion of Fe^{2+} through the glass filters used as diffusion barriers was measured in separate experiments (Fig. 2). Based on the experimental results the diffusion coefficients of radiolytic products and pertinent solutes were calculated assuming constant effective porosity and tortuosity. The diffusion coefficients used in the computer calculations are given in Table 2.

3.2 Radiolytic yield

The amount of H_2O_2 diffusing out of the irradiated volume was monitored by measuring the temporal build up of the H_2O_2 concentration in the outer aqueous phase. The experimental results are shown in Figs. 3-6.

The Fe^{2+} consumption in irradiated ground water with an initial Fe^{2+} concentration of $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3}$ is plotted in Fig. 7.

The radiolytic yields (G-values) calculated from the plots in Figs. 3-7 are summarized in Table 3.

The steady state concentration of H_2O_2 on the radiation-source side of the diffusion barrier estimated from the experimental data using Fick's first law

$$F = D \cdot A \cdot \epsilon \left(\frac{dc}{dx} \right) \quad (1)$$

where F = rate of transfer across diffusion barrier, A = area, ϵ = porosity and dc/dx = concentration gradient across diffusion barrier. The steady state concentrations obtained from the plots in Figs. 3-6 are given in Table 3.

4. COMPUTER CALCULATIONS

4.1 Computer program and yield of primary products

The computer program CHEMSIMUL has been described previously (Christensen and Bjergbakke 1986). The reactions, rate constants and primary yields (G-values) for α -radiolysis of water used in the calculations are given in Tables 4 and 5 respectively.

The reaction mechanism for the carbonate system was simplified to involve only CO_3^{2-} ions and $k_{80} = 1.7 \cdot 10^7$ was used to represent the overall rate constant for the reactions with both HCO_3^- and CO_3^{2-} .

4.2 Diffusion of reactants

The radiolytic products H_2 , O_2 and H_2O_2 are assumed to diffuse out of the irradiated volume through the filter and into the outer aqueous phase (see Fig. 1).

4.2.1 Diffusion to the inner phase

The temporal change in concentration within the irradiated volume $V(Irr)$ is given by the equation

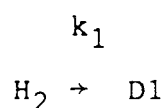
$$-dc/dt = F/V(Irr) = A \cdot D \cdot c / V(Irr) \cdot x \cdot 10^3$$

$V(Irr) = 1.81 \cdot 10^{-5} \text{ dm}^3$ and $D \text{ (cm}^2 \cdot \text{s}^{-1}\text{)}$ is the diffusivity in water

Assuming the thickness (x) of the inner phase to be 0.06 cm and the area A to correspond to the fictive area of a simplified linear case ($A = 11 \text{ cm}^2$) we obtain

$$-dc/dt = 1.01 \cdot 10^4 \cdot D \cdot c$$

In the computer program the diffusion must be described by rate equations. The diffusion of e.g. H_2 is thus handled by the equations



$$D1 \xrightarrow{k_2} H_2$$

$$-dc/dt = D \cdot 1.01 \cdot 10^4 c - k_2 \cdot D1$$

Also $D1 \cdot V(Irr) = c(In) \cdot V(In)$

where $V(In)$ = volume of inner aqueous phase

$c(In)$ = concentration in inner aqueous phase

Using the values given above, we obtain

$$D1 = 36.5 \cdot c(In)$$

$$dc/dt = 0 \text{ when } c(Irr) = c(In)$$

$$\text{i.e. } k_2 = k_1/36.5 = 36.5 \cdot D \cdot 1.01 \cdot 10^4 / 36.5 = 278 \cdot D$$

4.2.2 Diffusion through glass-filter into the outer aqueous phase

Diffusion out of the inner phase may be described by the equation

$$F = A \cdot \epsilon \cdot D \cdot dc(In)/dx$$

$$dc(In)/dt = -A \cdot \epsilon \cdot D \cdot c(In) / V(In) \cdot x \cdot 10^3$$

where A = 33 cm²
 D = diffusivity in filter (cm²·s⁻¹)
 (measured, see Table 2)
 V(In) = volume of inner phase (dm³)
 x = thickness of glassfilter (cm)
 ε = filter porosity

Using the values given in Table 2 we obtain

$$-dc(\text{In})/dt = 66 \cdot D \cdot c(\text{In}) \quad (\text{Filter 1})$$

$$-dc(\text{In})/dt = 15.2 \cdot c(\text{In}) \quad (\text{Filter 2})$$

or $-dc(\text{D1})/dt = 66 \cdot c(\text{D1})$

$$-dc(\text{D1})/dt = 15.2 \cdot c(\text{D1})$$

The diffusion may be thus expressed as a rate equation in the reaction mechanism i.e. D1 → D1A with rate constants 66·D or 15.2·D (for filter 1 and 2 respectively), using diffusivities pertinent to the glass filters.

It should be noted that the species D1 and D1A, although representing species in the inner and outer aqueous phases respectively in the calculations are treated as species in the irradiated volume.

4.2.3 Diffusion of solutes from the outer aqueous phase to the irradiated volume

In some experiments the solutions contained reactive solutes e.g. HCO_3^- , Cl^- , Fe^{2+} which may diffuse into the irradiated volume, if depleted in this volume.

Corresponding reactions and rate equations as given above were used to describe this diffusive transport.

5. RESULTS OF CALCULATION

5.1 Test calculations

Three methods of calculation were tested on water at pH 8, corresponding to case 1a, section 2.3.

a) As described above using the dose rate
 $(\text{DR}) = 73 \text{ rad}\cdot\text{s}^{-1}$

b) Calculation without diffusion, but using
 $\text{DR} = 73/36.5 = 2 \text{ rad}\cdot\text{s}^{-1}$

This method corresponds to a simplified case, where it is assumed that the α -radiation is absorbed in the inner phase (and not only in the irradiated phase, which is the real case). If this is a realistic case the diffusion

through the glass filter may easily be calculated.

- c) Calculation without diffusion using $DR = 73 \text{ rad}\cdot\text{s}^{-1}$ but corresponding to intermittent irradiation.

In this case it is assumed that the water of the inner phase is circulated through the irradiated phase, resulting in a case in which the real time is equal to 36.5 times the time of irradiation.

There are as can be seen in Table 6, some differences in the results obtained using the three methods. Method a is regarded as the most realistic one and this method, including equations for diffusion through the glass filter, was therefore used in the subsequent calculations.

The following yields were obtained: $G(\text{H}_2) = 1.27$;
 $G(\text{O}_2) = 0.13$; $G(\text{H}_2\text{O}_2) = 1.01$. The corresponding steady state concentrations in the inner phase were 6.8, 1,6 and 16.9 $\text{mol}\cdot\text{dm}^{-3}$ respectively.

5.2 Solutions 1a-1d

In the computer calculations no attempts were made to include equations to determine the delay in the break-through of H_2O_2 into the outer phase. The delay may be estimated assuming

$G(\text{H}_2\text{O}_2) = 1$. The time required to obtain steady state concentration for H_2O_2 in the inner aqueous phase is

$$(1.7 \cdot 10^{-5} \cdot 0.66 \cdot 10^9 / 73 \cdot 1.81 \cdot 10^{-2}) = 8.5 \cdot 10^3 \text{ s}$$

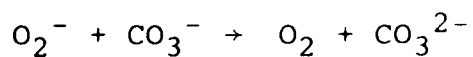
i.e. 2.4 h

and

$$(0.5 \cdot 33 \cdot 0.4 \cdot 0.53 \cdot 2.4) / 0.66 = 12.5 \text{ h}$$

is required to establish the concentration gradient across the filter. The delay obtained from the experimental break through curves is longer.

In the calculations of case 1a it was found that steady state concentrations in the inner phase were obtained in about 6 h. $G(\text{H}_2\text{O}_2)$ (H_2O_2 diffused into the outer phase) was 1.01 in fair agreement with the experimental value, 1.06, see Table 7 and Figure 8. The calculated $G(\text{H}_2\text{O}_2)$ values are almost the same (1.00) in solutions 1b (123 ppm HCO_3^-) and 1c (synthetic ground water), whereas the measured yields are lower, see Table 7. In solutions 1b and 1c $G(\text{O}_2)$ was found to be slightly higher than in solution 1a, probably because of the reaction



The Cl^- ion (1c) does not seem to have any effect, probably because of the fast back reaction



The similarity of the calculated results for solutions 1a, 1b and 1c may be understood by a close examination of Table 8, which compares the various reaction probabilities for OH and CO_3^- radicals.

For solution 1a an additional calculation was carried out in which it was assumed that the thickness of the inner volume was 0.06 cm instead of 0.02 cm (see Figure 1). The change in the inner volume did not result in changes in the G-values for H_2O_2 , H_2 or O_2 .

The reaction mechanism in solution 1d is rather complicated. It was found necessary to include the diffusion of Fe^{2+} and Fe^{3+} from the outer into the inner and irradiated phases. Reactions between Fe^{2+} and the H_2O_2 in the inner and outer phases were also included.

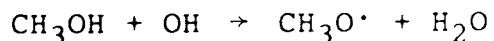
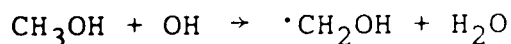
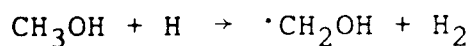
Fe^{2+} ions are quickly depleted in the irradiated and inner phases. The G-value for the disappearance of Fe^{2+} in the outer phase varies with time, see Figure 9. $G(-\text{Fe}^{2+})$ is 1.00 between 0 and 10 h; 1.41 between 10 and 20 h, and 1.07 between 20 and 30 h, much lower than the experimental value 3 ± 0.3 . However, in the calculations no term was included for the

oxidation of Fe^{2+} by O_2 , a reaction which may take place in the outer phase. Oxygen diffused into the outer phase with a G-value of 0.21, see Table 7.

For solution 1b a calculation was carried out assuming a rate constant of $1.5 \cdot 10^8 \text{ M}^{-1}\text{s}^{-1}$ for reaction 82. However, this did not change the yield of H_2O_2 , probably because the yield is determined mainly by the diffusion reactions.

5.3 Solution 2

In the irradiation of a 0.5 M aqueous solution of methanol (2a) a thicker glass filter was used, see Table 2. In addition to diffusion the following primary reactions were considered:



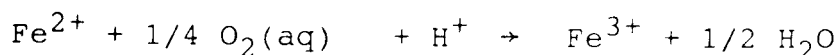
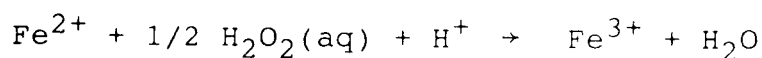
The subsequent reactions of the methanol radicals were not included in the calculations. The calculated $G(\text{H}_2\text{O}_2)$, 1.07, is in excellent agreement with the experimental value, (1.06 +/- 0.1).

6. DISCUSSION

The measured and calculated yields of H_2O_2 diffusing out of small α -irradiated volumes of water at pH 8 and $0.5 \text{ mol}\cdot\text{dm}^{-3}$ aqueous methanol solutions at pH 5 are in good agreement. On irradiation of $2\cdot 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ HCO_3^- solutions and synthetic ground water, containing HCO_3^- ($2\cdot 10^{-3}$) and Cl^- ($2\cdot 10^{-3}$) as principal reactive ions, $G(\text{H}_2\text{O}_2)$ decreased to 0.69 ± 0.03 as compared to 1.06 ± 0.1 for pure water. A corresponding decrease in $G(\text{H}_2\text{O}_2)$ was, however, not obtained by the computer calculations.

On addition of $2\cdot 10^{-6} \text{ mol}\cdot\text{dm}^{-3}$ Fe^{2+} to synthetic ground water Fe^{2+} was oxidized to Fe^{3+} at a rate corresponding to $G(-\text{Fe}^{2+}) = 3 \pm 0.3$, whereas $G(-\text{Fe}^{2+}) = 1.4$ was obtained by computer calculations. It should, however, be pointed out that the computer program calculates the yields of radiolysis products and reactive solutes diffusing out of respectively into the irradiated solution whereas the chemical analysis were carried out on samples taken from the bulk solution. The experimentally observed disappearance of Fe^{2+} is therefore caused not only by radiolytic reactions in the irradiated solution but also by slow reactions in the bulk phase.

Assuming the following reactions



an effective $G(-\text{Fe}^{2+})$ for the bulk solution is given by

$$G(-\text{Fe}^{2+})_{\text{eff}} = G(-\text{Fe}^{2+}) + 2 \cdot G(\text{H}_2\text{O}_2) + 4 \cdot G(\text{O}_2)$$

using the computed G-values given in Table 7, $G(-\text{Fe}^{2+})_{\text{eff}}$ is found to be 2.56 i.e. somewhat lower than the experimental value.

The discrepancy between calculated and experimental $G(\text{H}_2\text{O}_2)$ for solutions containing HCO_3^- ions may be due to incomplete description of the radiolytic reaction mechanism for the carbonate system or slow reactions in the bulk solution involving $\text{HCO}_3^-/\text{H}_2\text{O}_2$, leading to the formation of O_2 . The latter is difficult to envisage and a possible explanation is that the importance of the reaction $\text{H} + \text{HCO}_3^- \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2$ has been underestimated. A further decrease in the rate constant of reaction 82 below $1.5 \cdot 10^8$ could also make reaction 83 effective in decomposition of H_2O_2 . An increase in the rate constant of reaction 83 would have the same effect.

7. CONCLUSIONS

The formation of an expanding oxidative volume by the diffusion of radiolytically formed oxidizing species out of α -irradiated volumes of pure water and synthetic ground water containing HCO_3^- and Cl^- as principal reactive solutes has been demonstrated by monitoring the H_2O_2 production and Fe^{2+}

consumption in an outer aqueous phase separated from the irradiated solution by a diffusion barrier.

The experimental $G(\text{H}_2\text{O}_2)$ values obtained by irradiation of HCO_3^- containing solutions were not obtained by computer calculations, most probably due to inadequate description of the radiolytic reaction scheme for the carbonate system.

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Table 1

Composition of synthetic ground water (Allard solution)

Species	Conc mg·dm ⁻³
HCO ₃ ⁻	123
SO ₄ ²⁻	9.6
Cl ⁻	70
SiO ₂ (tot)	12
Ca ²⁺	18
Mg ²⁺	4.3
Na ⁺	65
K ⁺	3.9

Table 2

Diffusivities in water and glass filters used
as diffusion barriers.

Species	$D(\text{H}_2\text{O}) \cdot 10^{+6}$ $\text{cm}^2 \cdot \text{s}^{-1}$	$D(\text{Filter 1}) \cdot 10^{+6}$ $\text{cm} \cdot \text{s}^{-1}$	$D(\text{Filter 2}) \cdot 10^{+6}$ $\text{cm}^2 \cdot \text{s}^{-1}$

Fe^{2+}	12	1.23 ^{x)}	6.0 ^{x)}
HCO_3^-	13	1.3	6.3
Cl^-	13	1.3	6.3
H_2	60	5.9	29.0
O_2	25	2.5	12.2
H_2O_2	19	1.9	9.2

x) measured

Filter 1) Area 33 cm^2 , thickness 4 cm, porosity $\epsilon=0.53$

Filter 2) Area 33 cm^2 , thickness 2.8 cm, porosity $\epsilon=0.85$

Table 3

Experimental G-values^{x)} and steady state concentrations of H₂O₂ calculated from diffusion through glass filter.

Solution	G ^{x)} (H ₂ O ₂)	(H ₂ O ₂) mol·dm ⁻³
dist H ₂ O pH = 8 K ₂ HPO ₄ buffer (solution 1a)	1.06 +/- 0.1	1.72·10 ⁻⁵
2mM HCO ₃ ⁻ pH = 8 (solution 1b)	0.69 +/- 0.03	1.12·10 ⁻⁵
synthetic ground water (solution 1c)	0.69 +/- 0.03	1.12·10 ⁻⁵
synthetic ground water 2 m M Fe ²⁺ (solution 1d)	G(-Fe ²⁺) 3 +/- 0.3	

0.5M CH₃OH 1.06 +/- 0.1 1.55 · 10⁻⁵

pH = 5

(solution 2)

x)

G(molecules/100 eV)

Table 4

Reaction system and rate constants.

	Rate constant
	$M^{-1} s^{-1}$
RE1: $OH + OH = H_2O_2$	4 E9
RE2: $OH + E^- = OH^- + H_2O$	2 E10
RE3: $OH + H = H_2O$	2.5 E10
RE6: $OH + O_2^- = OH^- + O_2$	1 E10
RE9: $OH + H_2O_2^- = H_2O + O_2^- + H^+$	2.25 E7
RE12: $OH + H_2 = H_2O + H$	4 E7
RE19: $E^- + E^- = 2 \cdot OH^- + H_2$	5 E9
RE20: $E^- + H = OH^- + H_2$	2 E10
RE21: $E^- + HO_2 = HO_2^- + H_2O$	2 E10
RE22: $E^- + O_2^- = HO_2^- + OH^-$	1.2 E10
RE23: $E^- + H_2O_2 = OH + OH^- + H_2O$	1.6 E10
RE25: $E^- + H^+ = H + H_2O$	2.2 E10
RE26: $E^- + O_2 = O_2^- + H_2O$	2 E10
RE29: $E^- + H_2O = H + OH^- + H_2O$	2 E1
RE31: $H + H = H_2$	1 E10
RE32: $H + HO_2 = H_2O_2$	2 E10
RE33: $H + O_2^- = HO_2^-$	2 E10
RE34: $H + H_2O_2 = OH + H_2O$	6 E7
RE35: $H + OH^- = E^-$	2 E7
RE36: $H + O_2 = O_2^- + H^+$	2 E10
RE56: $HO_2 = O_2^- + H^+$	8 E5
RE57: $HO_2 + HO_2 = O_2 + H_2O_2$	7.5 E5

RE58:	$\text{HO}_2 + \text{O}_2^- = \text{O}_2 + \text{HO}_2^-$	8.5 E7
RE61:	$\text{O}_2^- + \text{H}^+ = \text{HO}_2$	5 E10
RE68:	$\text{H}_2\text{O}_2 + \text{OH}^- = \text{HO}_2^+ + \text{H}_2\text{O}$	5 E8
RE69:	$\text{HO}_2^- + \text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{OH}^-$	5.735 E4
RE73:	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	2.599 E-5
RE74:	$\text{H}_2\text{O} + \text{O}_2^{--} = \text{HO}_2^- + \text{OH}^-$	1
RE76:	$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	1.43 E11
RE80:	$\text{OH} + \text{CO}_3^{--} = \text{CO}_3^- + \text{OH}^-$	4 E7
RE82:	$\text{O}_2^- + \text{CO}_3^- = \text{CO}_3^{--} + \text{O}_2$	1.5 E9
RE83:	$\text{H}_2\text{O}_2 + \text{CO}_3^- = \text{CO}_3^{--} + \text{O}_2^- + 2 \cdot \text{H}^+$	8 E5
RE88:	$\text{CO}_2 + \text{OH}^- = \text{CO}_3^{--} + \text{H}^+$	1 E6
RE90:	$\text{H}_2\text{O} + \text{CO}_4^{--} = \text{CO}_3^{--} + \text{H}_2\text{O}_2$	1 E2
RE91:	$\text{CO}_3^- + \text{CO}_3^- = \text{CO}_4^{--} + \text{CO}_2$	6 E6
RE92:	$\text{CO}_3^- + \text{Fe}^{++} = \text{CO}_3^{--} + \text{Fe}^{+++}$	1 E8
RE105:	$\text{Fe}^{++} + \text{OH} = \text{Fe}^{+++} + \text{OH}^-$	3.4 E8
RE106:	$\text{Fe}^{++} + \text{E}^- = \text{Fe}^{+++} + \text{OH}^- + \text{H}^-$	1.2 E8
RE107:	$\text{Fe}^{+++} + \text{E}^- = \text{Fe}^{++} + \text{H}_2\text{O}$	2 E10
RE108:	$\text{Fe}^{++} + \text{H} = \text{Fe}^{+++} + \text{H}^-$	1.3 E7
RE109:	$\text{Fe}^{+++} + \text{H} = \text{Fe}^{++} + \text{H}^+$	1 E8
RE111:	$\text{Fe}^{++} + \text{O}_2^- = \text{Fe}^{+++} + \text{O}_2^{--}$	4 E8
RE112:	$\text{Fe}^{+++} + \text{O}_2^- = \text{Fe}^{++} + \text{O}_2$	4 E8
RE113:	$\text{Fe}^{++} + \text{H}_2\text{O}_2 = \text{Fe}^{+++} + \text{OH} + \text{OH}^-$	60
RE115:	$\text{H}^- + \text{H}_2\text{O} = \text{H}_2 + \text{OH}^-$	1
RE116:	$\text{O}_2^{--} + \text{H}_2\text{O} = \text{HO}_2^- + \text{OH}^-$	1
RE125:	$\text{OH} + \text{Cl}^- = \text{ClOH}^-$	4.3 E9
RE128:	$\text{E}^- + \text{Cl} = \text{Cl}^- + \text{H}_2\text{O}$	1 E10
RE129:	$\text{E}^- + \text{Cl}_2^- = 2\text{Cl}^- + \text{H}_2\text{O}$	1 E10
RE130:	$\text{E}^- + \text{ClOH}^- = \text{Cl}^- + \text{OH}^- + \text{H}_2\text{O}$	1 E10
RE132:	$\text{E}^- + \text{Cl}_2 = \text{Cl}_2^- + \text{H}_2\text{O}$	1 E10

RE133: $E^- + Cl_3^- = Cl_2^- + Cl^- + H_2O$	1 E10
RE136: $H + Cl = Cl^- + H^+$	1 E10
RE137: $H + Cl_2^- = 2Cl^- + H^+$	8 E9
RE138: $H + ClOH^- = Cl^- + H_2O$	1 E10
RE139: $H + Cl_2 = Cl_2^- + H^+$	7 E9
RE141: $H + Cl_3^- = Cl_2^- + Cl^- + H^+$	1 E10
RE143: $O_2^- + Cl_2 = Cl_2^- + O_2$	1 E9
RE144: $O_2^- + Cl_3^- = Cl_2^- + Cl^- + O_2$	1 E9
RE145: $O_2^- + Cl_2^- = 2Cl^- + O_2$	1.2 E10
RE147: $H_2O_2 + Cl_2^- = 2Cl^- + O_2^- + 2H^+$	1.4 E5
RE148: $H_2O_2 + Cl_2 = HO_2 + Cl_2^- + H^+$	1.9 E2
RE150: $OH^- + Cl_2^- = ClOH^- + Cl^-$	7.3 E6
RE152: $H^+ + ClOH^- = Cl + H_2O$	2.1 E10
RE158: $Cl^- + Cl = Cl_2^-$	2.1 E10
RE159: $Cl^- + ClOH^- = Cl_2^- + OH^-$	9 E4
RE161: $Cl^- + Cl_2 = Cl_3^-$	1 E4
RE162: $ClOH^- = OH + Cl^-$	6.1 E9
RE163: $Cl_2^- = Cl + Cl^-$	1.1 E5
RE164: $Cl_2^- + Cl_2^- = Cl_3^- + Cl^-$	7 E9
RE165: $Cl_3^- = Cl_2 + Cl^-$	5 E4
RE170: $Cl + Fe^{++} = Fe^{+++} + Cl^-$	1.05 E10
RE171: $ClOH^- + Fe^{++} = Fe^{+++} + Cl^- + OH^-$	1 E8
RE172: $Cl_2^- + Fe^{++} = Fe^{+++} + 2Cl^-$	1 E7
RE173: $Cl_2 + Fe^{++} = Fe^{+++} + Cl_2^-$	80
RE175: $Cl_3^- + Fe^{++} = Fe^{+++} + Cl_2^- + Cl^-$	2 E5
RE200: $H_2 = DUMMY 1$	6.06 E-1
RE201: $O_2 = DUMMY 2$	2.52 E-1
RE202: $H_2O_2 = DUMMY 3$	1.21 E-1
RE203: $DUMMY 1 = H_2$	1.67 E-2

RE204: DUMMY 2 = O ₂	6.95 E-3
RE205: DUMMY 3 = H ₂ O ₂	3.34 E-3
RE206: DUMMY 1 = DUMMY 1A	3.894 E-4
RE207: DUMMY 2 = DUMMU 2A	1.65 E-4
RE208: DUMMY 3 = DUMMY 3A	1.254 E-4
RE209: Fe ⁺⁺ = DUMMY 4	1.24 E-1
RE210: DUMMY 4 = Fe ⁺⁺	3.42 E-3
RE211: DUMMY 4 = DUMMY 4A	8.12 E-5
RE212: DUMMY 4A = DUMMY 4	4.87 E-7
RE213: Fe ⁺⁺⁺ + H ₂ O = DUMMY 5 + H ⁺	2.24 E-3
RE214: DUMMY 5 = Fe ⁺⁺⁺ + OH ⁻	3.42 E-3
RE215: DUMMY 5 = DUMMY 5A	8.12 E-5
RE216: DUMMY 3 + DUMMY 4 = DUMMY 5 + A	1.7
RE217: A + DUMMY 4 = DUMMY 5	1 E6
RE218: DUMMY 3A + DUMMY 4A = DUMMY 5A + B	1 E-2
RE219: B + DUMMY 4A = DUMMY 5A	1 E6
RE220: DUMMY 5A = DUMMY 5	4.87 E-7

Table 5Primary G-values for α -radiolysis of water.

G							
-H ₂ O	H ₂	H	e ⁻ _{aq}	H ₂ O ₂	HO ₂	OH	H ⁺
2.71	1.3	0.21	0.06	0.985	0.22	0.24	0.06

Table 6

Results of test calculations (see text for explanation)

	Concentration μM at $7.3 \cdot 10^3\text{s}$			Concentration μM at $3.65 \cdot 10^4\text{s}$		
	Method			Method		
	a	b	c	a	b	c
H ₂	19	18	19	91	88	92
O ₂	1.8	1.1	1.6	6	2	6
H ₂ O ₂	16	16	16	80	83	81

Table 7

Calculated steady state concentrations and G-values
for H₂, O₂ and H₂O₂

Case	Steady state concentrations, M, in inner phase			Calculated G-values			Measured G-values	
	H ₂	O ₂	H ₂ O ₂	H ₂	O ₂	H ₂ O ₂	H ₂ O ₂	
1a	6.8	1.6	16.9	1.27	0.13	1.01	1.06	+/- 0.1
1b	6.9	1.9	16.5	1.30	0.15	1.00	0.69	+/- 0.03
1c	6.9	1.9	16.3	1.30	0.15	1.00	0.69	+/- 0.03
1d	6.9	2.8	14.1	1.30	0.21	0.16 ^{x)}	-	
2	7.3	1.2	15.8	1.53	0.11	1.07	1.06	+/- 0.1

x)

G(-Fe²⁺) after 10 h: calculated 1.4; measured 3 +/- 0.3.

Table 8

Competing reactions

Solution 1a. Reactions of OH

	$c \cdot 10^6$	$k \cdot 10^{-7}$	$k \cdot c$
H ₂	7	4	280
H ₂ O ₂	17.5	2.25	390
O ₂ ^{·-}	0.30	1000	3000
OH	6 E-6	4000	2.4 E-2

Solution 1b. Reactions of OH

	$c \cdot 10^6$	$k \cdot 10^{-7}$	$k \cdot c$
H ₂	7	4	280
H ₂ O ₂	17	2.25	380
O ₂ ^{·-}	0.25	1000	2500
CO ₃ ²⁻	2000	1.7	34000

Solution 1c. Reactions of $\text{CO}_3^{\cdot-}$

	$c \cdot 10^6$	$k \cdot 10^{-6}$	$k \cdot c$
H_2O_2	17	0.8	14
O_2^-	0.25	1500	375
$\text{CO}_3^{\cdot-}$	5 E-5	6	3 E-4
$\text{O}_2^{\cdot-}$	0.25	150	38

Figure legends

- Fig. 1 Schematic drawing of irradiation cell with diffusion barrier.
- Fig. 2 Diffusion of Fe^{2+} through glass-filter.
 $D = l^2/6 \cdot t_c = 1.23 \cdot 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$.
 D from slope $6.14 \cdot 10^{-7}$
 porosity: 0.50 (from wt 0.53).
- Fig. 3 α -irradiated H_2O_2 production in $0.5 \text{ mol} \cdot \text{dm}^{-3}$ CH_3OH solution. pH = 5 (HClO_4)
 (diffusion barrier: $\epsilon = 0.85$, $X = 2.8$).
- Fig. 4 H_2O_2 production in α -irradiated H_2O .
 (K_2HPO_4 -buffer, pH 8).
- Fig. 5 H_2O_2 production in α -irradiated $2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ HCO_3^- solution (pH 8).
- Fig. 6 H_2O_2 production in α -irradiated synthetic ground water.
- Fig. 7 Fe(II) . Consumption by oxidizing species from α -irradiated synthetic ground water.
- Fig. 8 Calculated amount of H_2O_2 diffusing through glass-filter on α -radiolysis of water at pH 8 (solution 1a).

Fig. 9 Calculated concentration of Fe^{2+} on
 α -radiolysis of synthetic ground water
initially containing $2 \cdot 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \text{ Fe}^{2+}$
(solution 1d).

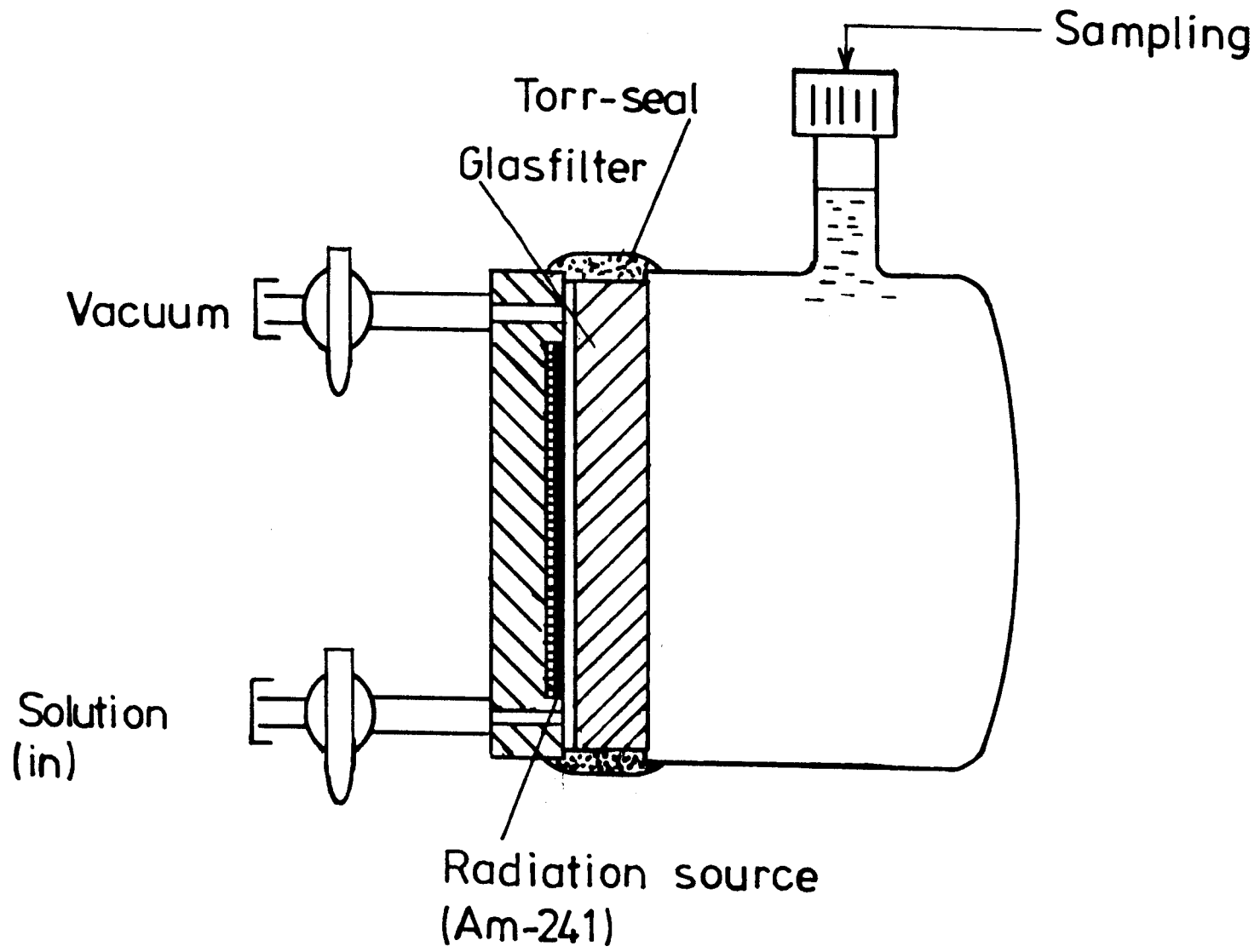


Fig. 1

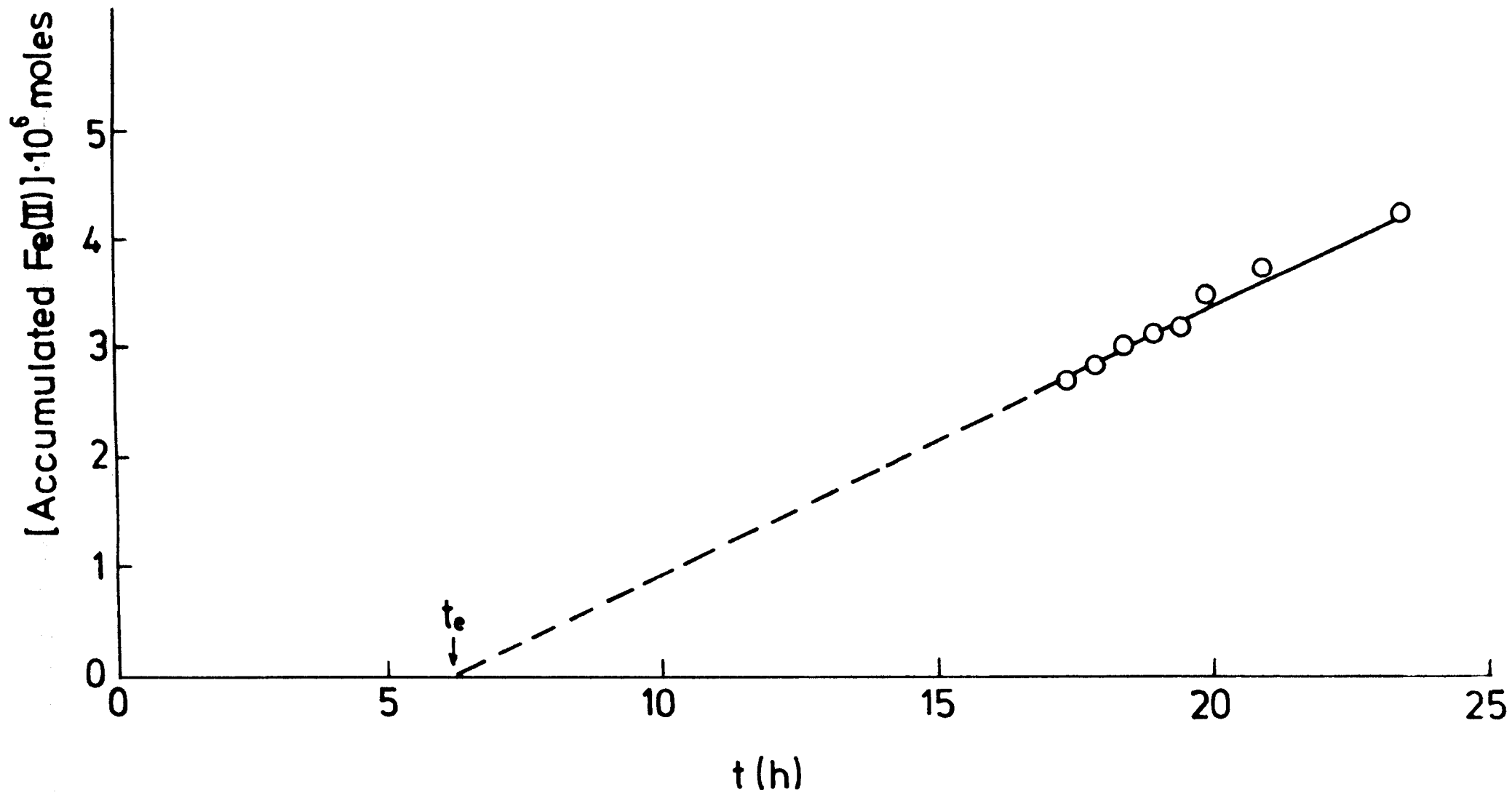


Fig. 2

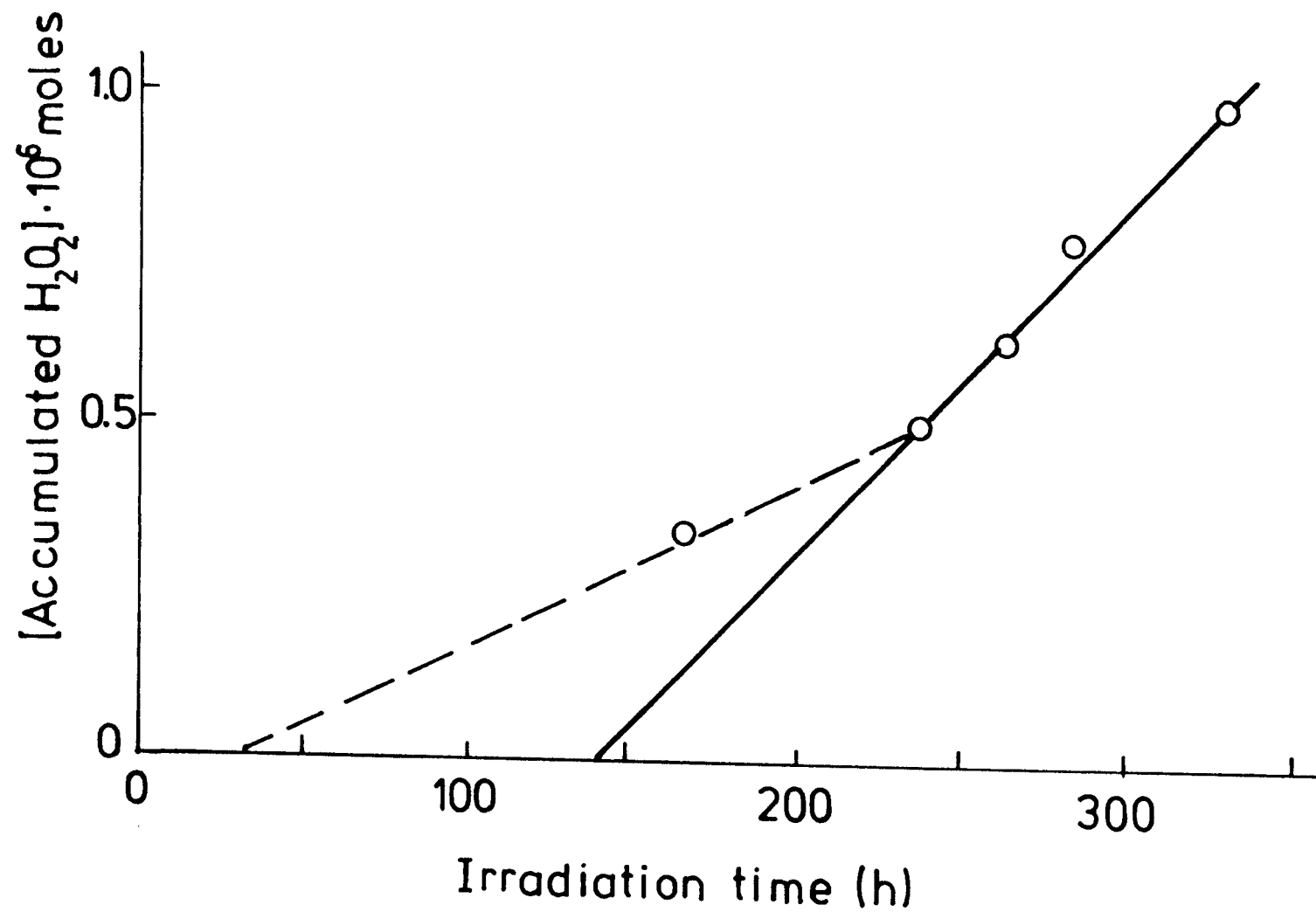


Fig. 3

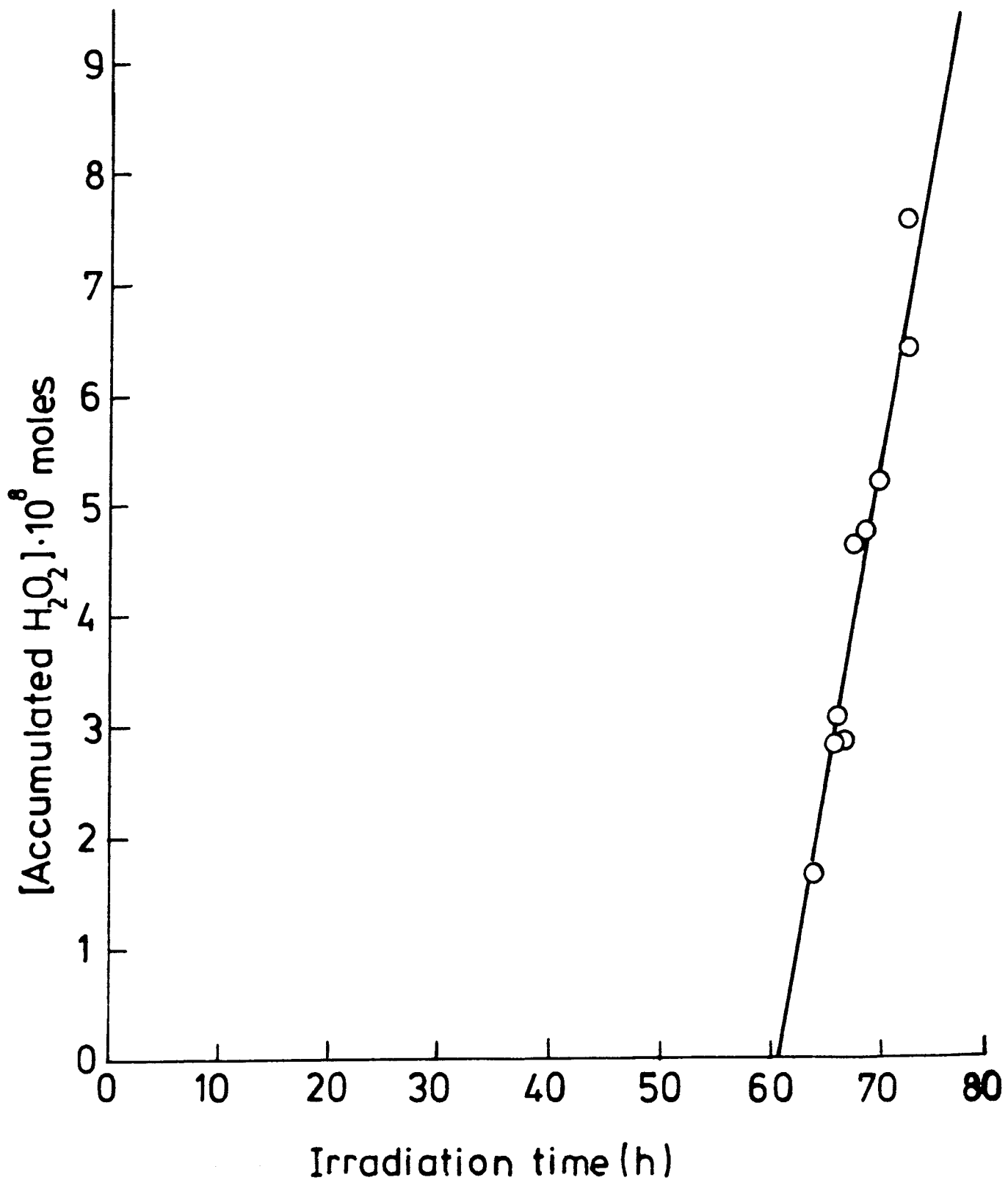


Fig. 4

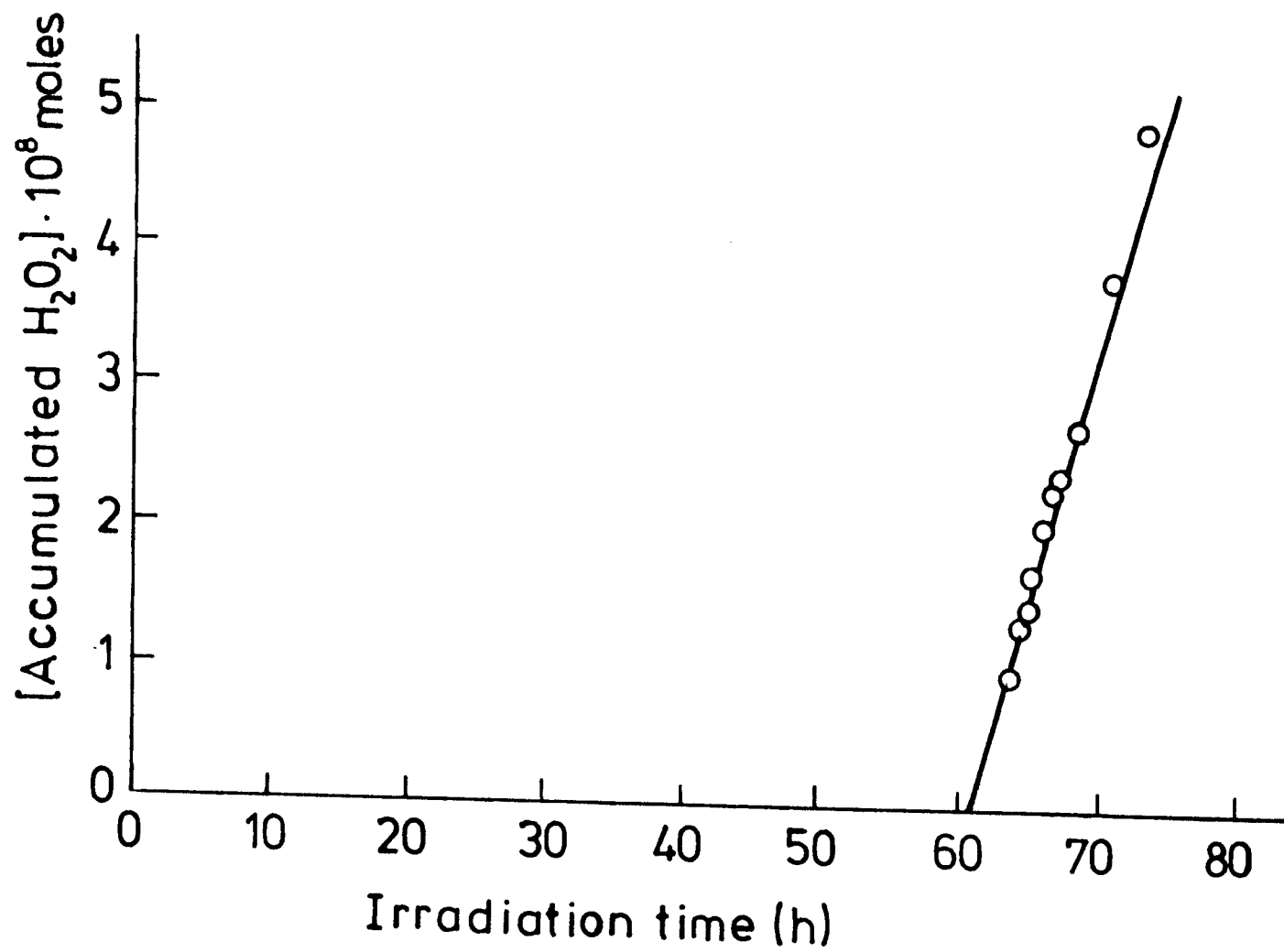


Fig. 5

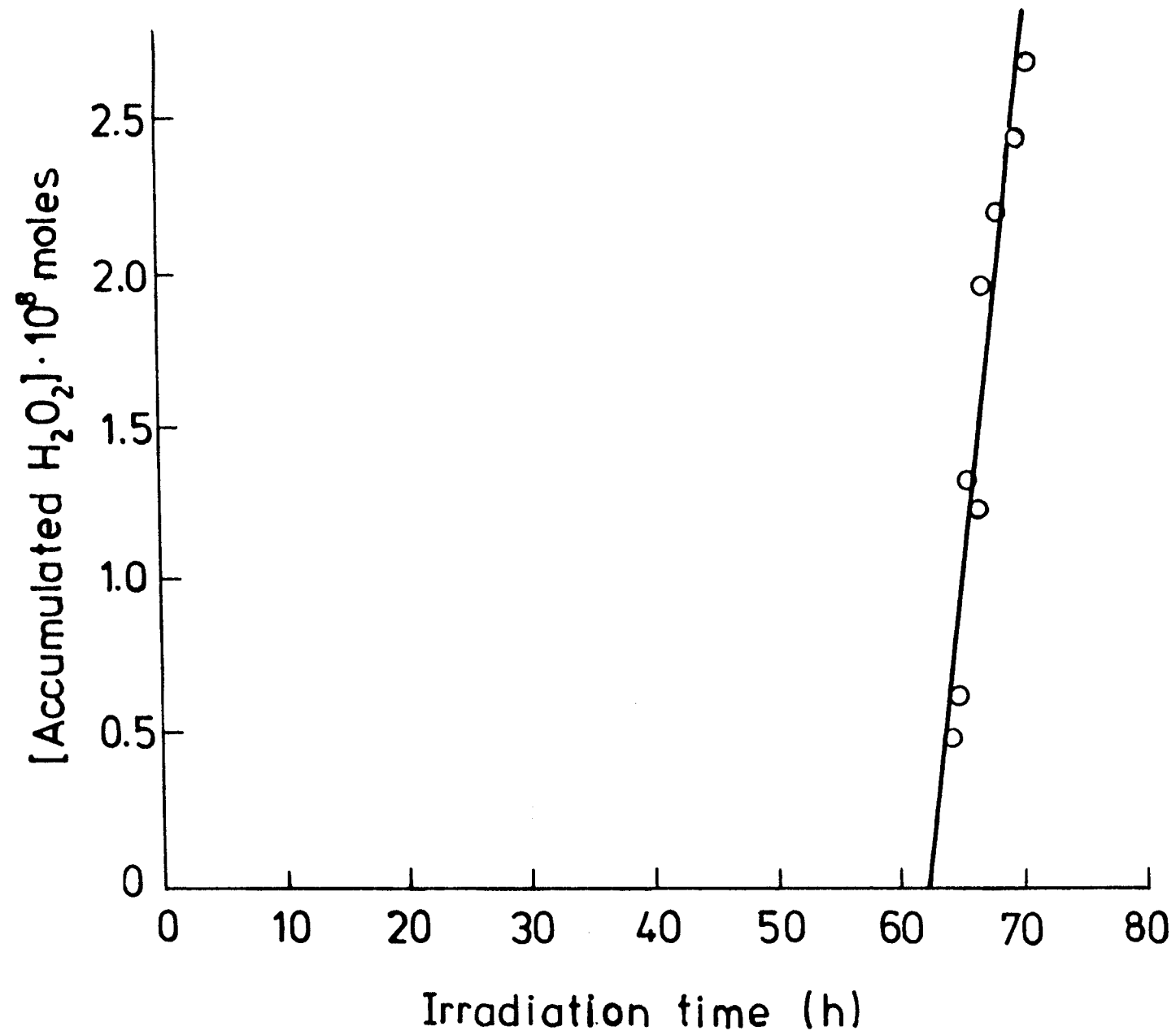


Fig. 6

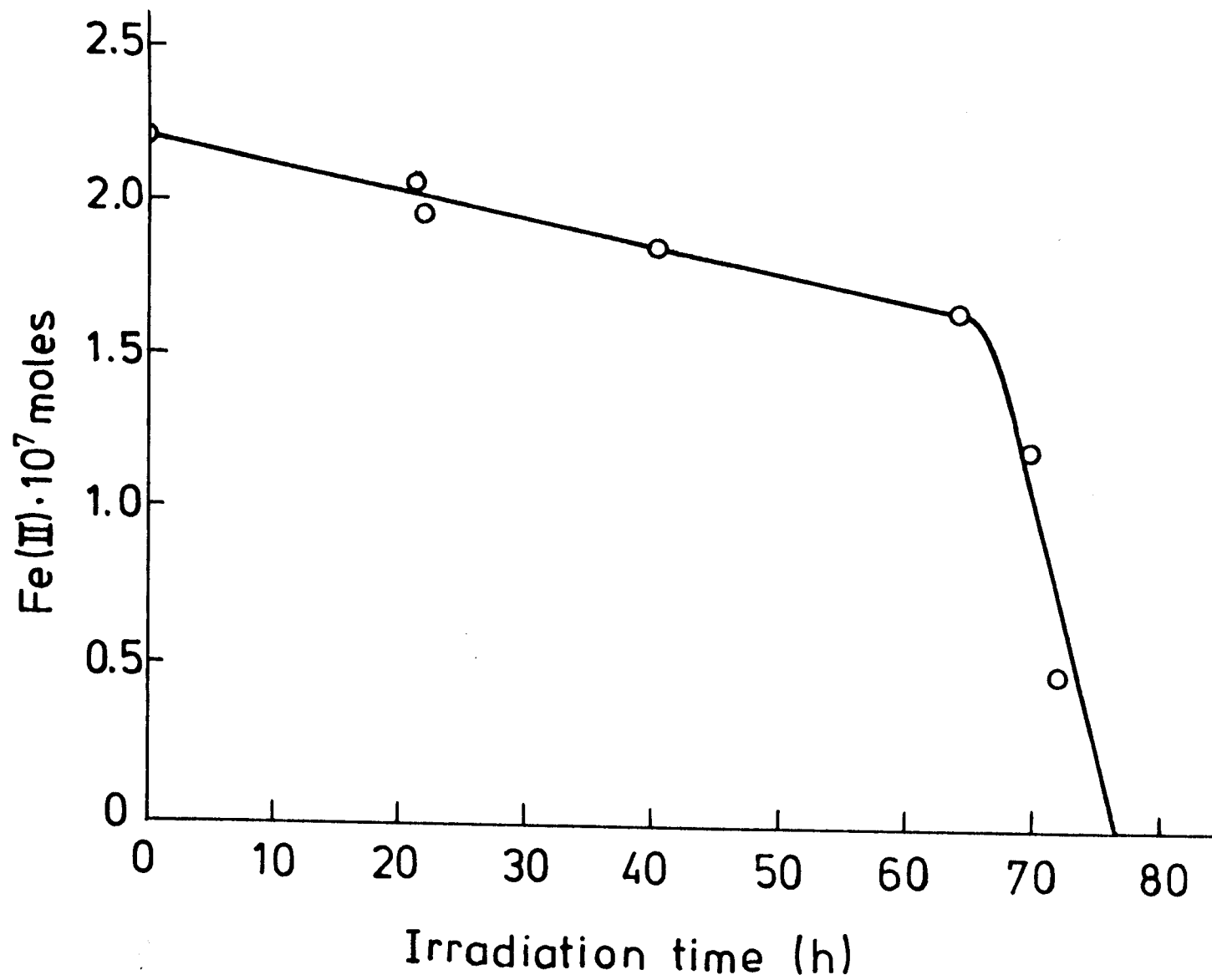


Fig. 7

DATE: 1988/01/27 TIME: 15:50:40

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-7

10

x — SCALE NO. 1: 0.0000181*DUMMY3A

5

4

3

2

1

0

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TIME IN SECS

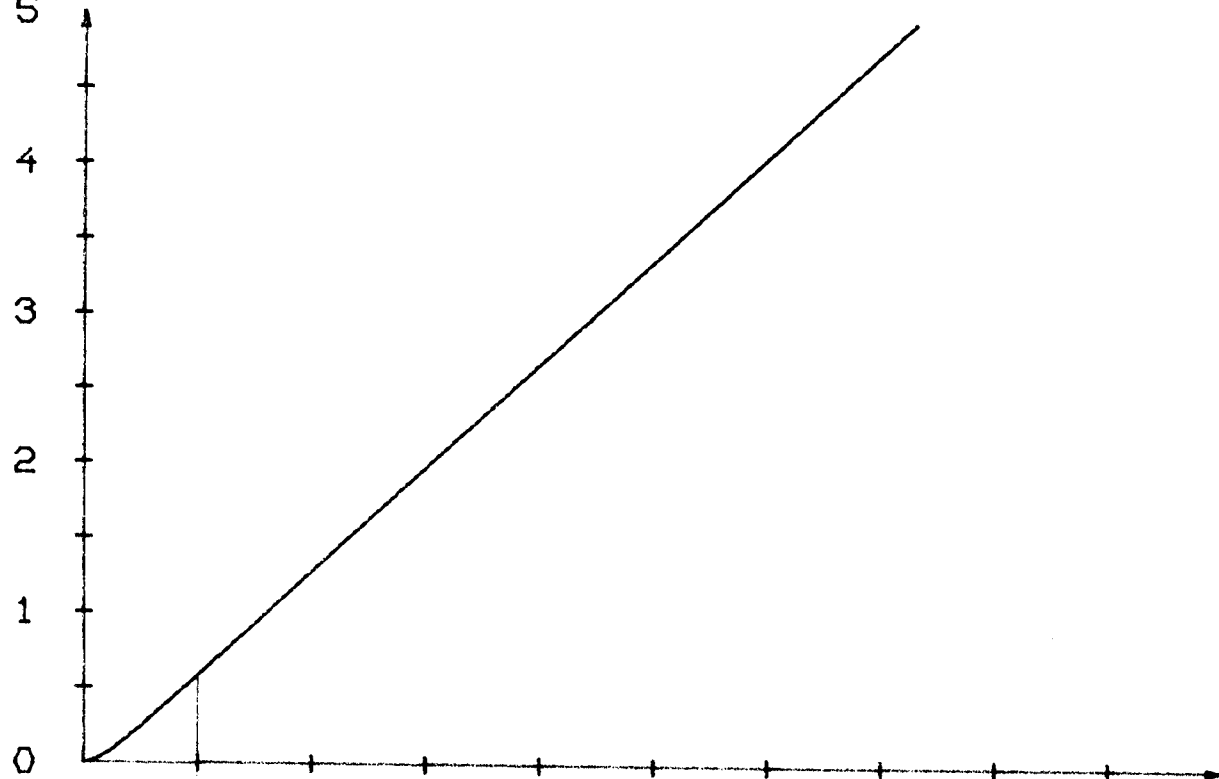


Fig. 8

DATE: 1988/02/04 TIME: 11:11:20

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TIME IN SECS

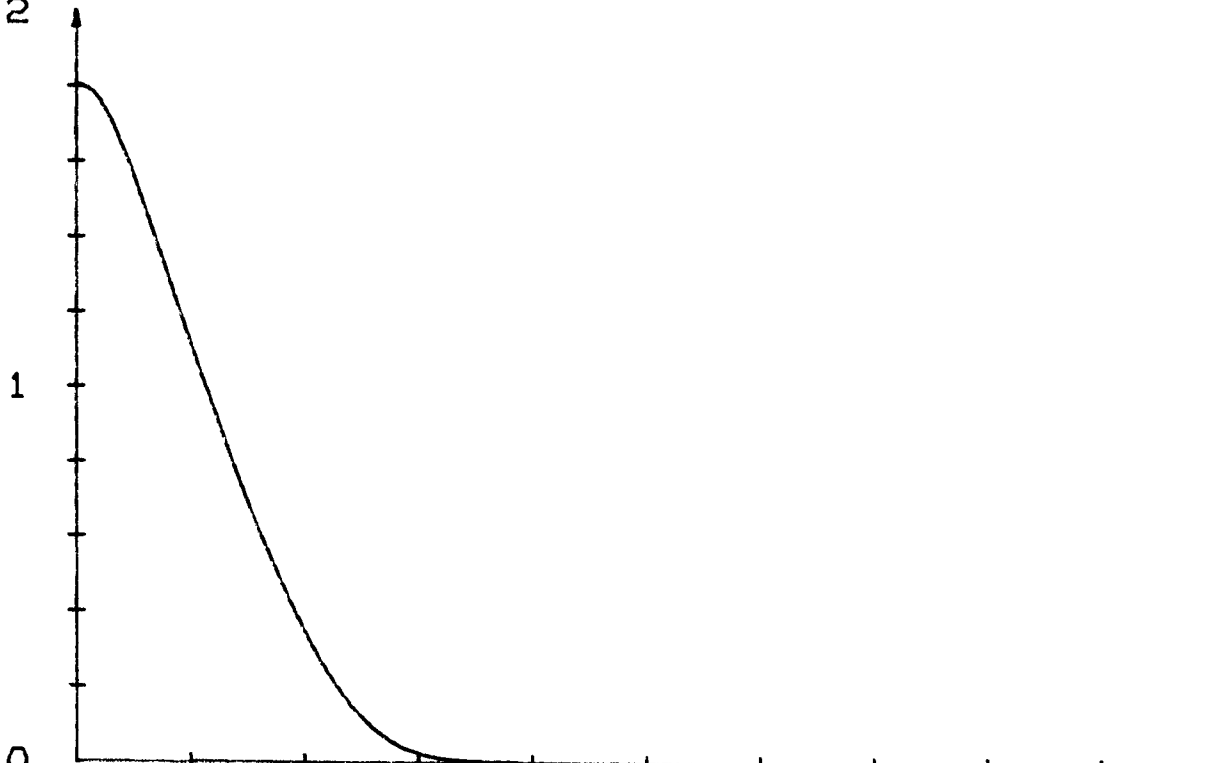


Fig. 9

List of SKB reports

Annual Reports

1977-78

TR 121

KBS Technical Reports 1 – 120.

Summaries. Stockholm, May 1979.

1979

TR 79-28

The KBS Annual Report 1979.

KBS Technical Reports 79-01 – 79-27.

Summaries. Stockholm, March 1980.

1980

TR 80-26

The KBS Annual Report 1980.

KBS Technical Reports 80-01 – 80-25.

Summaries. Stockholm, March 1981.

1981

TR 81-17

The KBS Annual Report 1981.

KBS Technical Reports 81-01 – 81-16.

Summaries. Stockholm, April 1982.

1982

TR 82-28

The KBS Annual Report 1982.

KBS Technical Reports 82-01 – 82-27.

Summaries. Stockholm, July 1983.

1983

TR 83-77

The KBS Annual Report 1983.

KBS Technical Reports 83-01 – 83-76

Summaries. Stockholm, June 1984.

1984

TR 85-01

Annual Research and Development Report 1984

Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01–84-19)

Stockholm June 1985.

1985

TR 85-20

Annual Research and Development Report 1985

Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01-85-19)

Stockholm May 1986.

1986

TR 86-31

SKB Annual Report 1986

Including Summaries of Technical Reports Issued during 1986

Stockholm, May 1987

1987

TR 87-33

SKB Annual Report 1987

Including Summaries of Technical Reports Issued during 1987

Stockholm, May 1988

Technical Reports

1988

TR 88-01

Preliminary investigations of deep ground water microbiology in Swedish granitic rocks

Karsten Pedersen

University of Göteborg

December 1987

TR 88-02

Migration of the fission products strontium, technetium, iodine, cesium and the actinides neptunium, plutonium, americium in granitic rock

Thomas Ittner¹, Börje Torstenfelt¹, Bert Allard²

¹Chalmers University of Technology

²University of Linköping

January 1988

TR 88-03

Flow and solute transport in a single fracture. A two-dimensional statistical model

Luis Moreno¹, Yvonne Tsang², Chin Fu Tsang²,

Ivars Neretnieks¹

¹Royal Institute of Technology, Stockholm, Sweden

²Lawrence Berkeley Laboratory, Berkeley, CA, USA

January 1988

TR 88-04

Ion binding by humic and fulvic acids: A computational procedure based on functional site heterogeneity and the physical chemistry of polyelectrolyte solutions

J A Marinsky, M M Reddy, J Ephraim, A Mathuthu

US Geological Survey, Lakewood, CA, USA

Linköping University, Linköping

State University of New York at Buffalo, Buffalo, NY, USA

April 1987

TR 88-05

Description of geophysical data on the SKB database GEOTAB

Stefan Sehlstedt

Swedish Geological Co, Luleå

February 1988

TR 88-06

Description of geological data in SKBs data-base GEOTAB

Tomas Stark
Swedish Geological Co, Luleå
April 1988

TR 88-07

Tectonic studies in the Lansjärv region

Herbert Henkel
Swedish Geological Survey, Uppsala
October 1987

TR 88-08

Diffusion in the matrix of granitic rock. Field test in the Stripa mine. Final report.

Lars Birgersson, Ivars Neretnieks
Royal Institute of Technology, Stockholm
April 1988

TR 88-09

The kinetics of pitting corrosion of carbon steel. Progress report to June 1987

G P Marsh, K J Taylor, Z Sooi
Materials Development Division
Harwell Laboratory
February 1988

TR 88-10

**GWHRT – A flow model for coupled groundwater and heat flow
Version 1.0**

Roger Thunvik¹, Carol Braester²
¹ Royal Institute of Technology, Stockholm
² Israel Institute of Technology, Haifa
April 1988

TR 88-11

**Groundwater numerical modelling of the Fjällveden study site – Evaluation of parameter variations
A hydrocoin study – Level 3, case 5A**

Nils-Åke Larsson¹, Anders Markström²
¹ Swedish Geological Company, Uppsala
² Kemakta Consultants Co, Stockholm
October 1987

TR 88-12

Near-distance seismological monitoring of the Lansjärv neotectonic fault region

Rutger Wahlström, Sven-Olof Linder,
Conny Holmqvist
Seismological Department, Uppsala University,
Uppsala
May 1988

TR 88-13

Validation of the rock mechanics HNFEMP code against Colorado school of mines block test data

Ove Stephansson, Tomas Savilahti
University of Luleå, Luleå
May 1988

TR 88-14

Validation of MUDEC against Colorado school of mines block test data

Nick Barton, Panayiotis Chryssanthakis,
Karstein Monsen
Norges Geotekniske Institutt, Oslo, Norge
April 1988

TR 88-15

Hydrothermal effects on montmorillonite. A preliminary study

Roland Pusch
Ola Karnland
June 1988

TR 88-16

Swedish Hard Rock Laboratory First evaluation of preinvestigations 1986-87 and target area characterization

Gunnar Gustafson
Roy Stanfors
Peter Wikberg
June 1988

TR 88-17

On the corrosion of copper in pure water

T E Eriksen¹, P Ndalamba¹, I Grenthe²
¹The Royal Institute of Technology, Stockholm
Department of nuclear chemistry
²The Royal Institute of Technology, Stockholm
Department of inorganic chemistry
March 1988

TR 88-18

Geochemical modelling of the evolution of a granite-concrete-water system around a repository for spent nuclear fuel

Bertrand Fritz, Benoit Madé, Yves Tardy
Université Louis Pasteur de Strasbourg
April 1988

TR 88-19

A Bayesian nonparametric estimation of distributions and quantiles

Kurt Pörn
Studsvik AB
November 1988

TR 88-20

**Creep properties of welded joints in OFHC
copper for nuclear waste containment**

Bo Ivarsson, Jan-Olof Österberg
Swedish Institute for Metals Research
August 1988

TR 88-21

**Modelling uranium solubilities in aqueous
solutions: Validation of a thermodynamic
data base for the EQ3/6 geochemical codes**

I Puigdomenech¹, J Bruno²

¹ Studsvik Nuclear, Nyköping
Environmental Services

² Royal Institute of Technology, Stockholm
Department of Inorganic Chemistry

October 1988