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Effects of β -radiolysis on the products from α -radiolysis of ground water

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 α -RADIOLYSIS OF GROUND WATER

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This report concerns a study which was conducted for SKBF/KBS. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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ABSTRACT

In a previous study it has been shown that α -radiolysis of a thin water film on spent fuel stored in a copper canister may result in formation of substantial amounts of hydrogen and oxygen.

In the present investigation the effect of low LET radiation, such as γ - and β -radiations, on these molecules when they diffuse out of the α -irradiated layer has been calculated using a computerized radiation chemical program. It has been found that low LET radiation under certain conditions may act as a recombiner for hydrogen and oxygen produced by α -radiolysis.

The effect of γ -radiation outside the canister is small - due to the low dose rates prevailing there. However, the relatively high β -radiation field existing inside the fuel cladding recombines the major part of the hydrogen and oxygen produced by α -radiolysis of pure water, in particular if the gases have to diffuse out through bentonite.

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1 INTRODUCTION

In a previous report the production of hydrogen and oxygen from radiolysis of water exposed to mainly α -radiation originating from spent fuel has been calculated (1). The water was assumed to have penetrated the copper canister and fuel cladding and then to exist as a 30 μm thin surface film on the fuel pellets. The contribution of β -radiation to the total dose in the film was around 25 %.

Under certain conditions substantial amounts of hydrogen could be evolved, according to the calculations (1). The conditions which led to the highest productions were

1. Irradiation of pure water, i e absence of iron ions and
2. Irradiation of water with a continuous supply of Fe^{2+} ions.

After diffusion out of the film the hydrogen and oxygen will be exposed to low-LET*-radiation (β and γ) and the molecules may recombine to a certain extent. The calculations presented here were carried out in order to determine the extent of this recombination in the two cases quoted above.

* LET: Linear Energy Transfer

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2 CONDITIONS

2.1 Computer program

The computer program previously described (1, 2) was used.

2.2 Dose rates

The dose rates previously given (1, 3) have been used: In the case of radiolysis inside the fuel cladding (1) the dose rates given in Table 1 have been used. In the case of radiolysis outside the copper cannister (3) the dose rates given in Table 2 have been used.

2.3 G-values

G-values applicable for γ - and β -radiation have been used, see Table 3.

The hydrogen and oxygen diffusing out of the thin α -irradiated water film are additional source terms, which in the present calculations have been transformed into G-values taking into account the amount of gas produced in the α -irradiated layer, the volume of the β -irradiated water and the dose rates in this water.

2.4 Iron-ions

As previously shown (1) Fe^{2+} ions play an important role in the mechanism and affect the radiolysis. In one of the scenarios treated here it has been assumed that Fe^{2+} ions are supplied continuously from the surrounding bentonite layer so that the Fe^{2+} concentration is maintained at a constant of 8.9×10^{-5} M, in agreement with one specific case from the previous calculations (1).

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2.5 Cases considered

1. Pure water
2. Water with a continuous supply of Fe^{2+} ions

For each of these main cases the following sub-cases A-D have been treated.

Case	Irradiation inside or outside the fuel	Water volume, l	Diffusion coeffi- cient applicabile for	Canister thickness cm
A	Inside	10	Water	-
B	Inside	10	Bentonite	-
C	Outside	180	Bentonite	1
D	Outside	180	Bentonite	10

For hydrogen D_{eff} is equal to 2×10^{-11} m^2/s in bentonite and 1.4×10^{-8} m^2/s in water. Corresponding values for oxygen are 2×10^{-11} and 5×10^{-9} m^2/s , respectively.

The supply of hydrogen in the two main cases is given in Table 4. These values are taken from Table 15 (pure water) and Table 13 (iron addition) from reference 1.

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3 RESULTS

3.1 Irradiation of pure water

3.1.1 Case 1A

In Table 5 the results of β -radiolysis of 10 l water inside the fuel cladding are presented. The production of hydrogen is equal to the amount of hydrogen which diffuses out of the system. It was assumed that hydrogen and oxygen diffused out of the system at a rate corresponding to their diffusion in water.

The integrated production can be compared with the integrated production in the thin α -irradiated layer, see Table 5. It can be seen that the β -irradiation outside this layer causes a considerable amount of recombination.

From Figure 1 it can be seen that equilibrium concentrations are established quickly for H_2 and O_2 . Hydrogen and oxygen are produced in stoichiometric amounts.

3.1.2 Case 1B

This case is the same as case 1A except that hydrogen and oxygen diffuse out through bentonite instead of through water. In period 6, i.e. after 100 000 y, it took a long time (about 30 y and several calculations) to establish equilibrium concentrations of hydrogen and oxygen, see Figure 2. This may be due to a combination of a relatively high G-value for hydrogen production, a low dose rate and a low diffusion constant.

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The production rates and integrated production are much smaller than in case 1A. The hydrogen and oxygen produced in the thin α -irradiated layer are recombined to a large extent. This is because the molecules - due to their slow diffusion in bentonite - remain a longer time in the β -irradiated layer.

3.1.3 Case 1C

In this case recombination from γ -radiolysis outside the canister is considered. The canister thickness is 1 cm and the water volume is 180 l. The dose rates outside the container are several times lower than inside the fuel cladding. This means that the G-values calculated from the production of H_2 and O_2 in the thin α -irradiated layer become very large, and consequently the recombination outside the container becomes very small. The results are shown in Table 6. It takes more than 100 y to establish equilibrium, see Figure 3.

From Table 6 it can be seen that the integrated production after 1 million years is 29 000 mol, the same as the production in the thin α -irradiated layer. This means that recombination is negligible.

3.1.4 Case 1D

This case is the same as case 1C except that the canister thickness is 10 cm.

From Table 6 it can be seen that in this case also recombination is negligible.

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3.2 Irradiation of water with a continuous supply of Fe^{2+}

Stoichiometric amounts of hydrogen and oxygen are assumed to be supplied from the α -irradiated layer.

3.2.1 Case 2A

β -radiolysis of 10 l water inside the fuel cladding is considered. Diffusion takes place in water. The production of hydrogen in the various time periods and integrated production are shown in Table 7. Stoichiometric amounts of Fe^{3+} are formed.

By comparison with the hydrogen production in the thin α -irradiated layer (Table 7, last column) it can be seen that β -irradiation in the presence of Fe^{2+} ions increases the hydrogen production, i e hydrogen is also produced by the β -radiation.

3.2.2 Case 2B

β -radiolysis of 10 l water inside the fuel cladding is considered. Diffusion takes place in bentonite. As can be seen from Table 7 more than half of the hydrogen, which diffuses out of the thin α -irradiated film is recombined in the β -irradiated film.

3.2.3 Case 2C

In this case recombination from γ -radiolysis outside the canister is considered. The canister thickness is 1 cm and the water volume is 180 l. As can be seen from Table 8 in this case recombination takes place to a small extent.

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3.2.4 Case 2D

This case is equal to case 2C except that the canister thickness is 10 cm.

As can be seen from Table 8 in this case there is no reduction in the hydrogen production.

3.2.5 Case 3A

β -radiolysis of 10 l water inside the fuel assuming that only hydrogen diffuses out of the α -irradiated layer. Diffusion takes place through water. The results are shown in Table 9. It can be seen that the hydrogen production is somewhat higher than in case 2A, where it was assumed that stoichiometric amounts of hydrogen and oxygen were supplied from the α -irradiated layer. Case 3A may be a more realistic case than case 2A, because oxygen is probably consumed by Fe^{2+} ions in the α -irradiated layer. However, the effect is not very large.

3.2.6 Case 3B

This case is equal to case 3A except that diffusion takes place through bentonite. The hydrogen production is considerably higher than in case 2B, see Table 9.

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4 CONCLUSIONS

Low LET radiation such as γ -and β -radiations may, under certain conditions, act as a re-combiner for hydrogen and oxygen produced by α -radiolysis of a 30 μm thin water film which could exist on the fuel surfaces.

The effect of γ -radiation outside the canister is small - due to the low dose rates prevailing there. However, the relatively high β -radiation field existing inside the fuel cladding recombine the major part of the hydrogen and oxygen produced by the α -radiolysis of pure water, in particular if the gases have to diffuse out through bentonite.

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Table 1

β -Dose rates on the surface of fuel pellets after various storage times. BWR fuel with a burn-up of 33 Mwd/kg.

Dose rate in rad/s after various storage times in y							
Storage time	40	100	300	1000	10 ⁴	10 ⁵	10 ⁶
Dose rate	10	6.9	4.5	2.1	0.45	1.7E-2	9E-3

Table 2

γ -Dose rates in rad/s absorbed in 180 l water outside the fuel canister. BWR fuel with a burn-up of 33 Mwd/kg.

Time, year	canister thickness, cm	
	1	10
40-60	0.37	1.31E-3
60-100	0.19	5.58E-4
100-300	2.6E-2	7.41E-5
300-600	6.8E-4	2.66E-6
600-E3	1.7E-4	8.6E-7
E3-3E3	1.1E-4	6.8E-7
3E3-E4	1.5E-4	5.7E-7
E4-3E4	1.5E-4	8.0E-7
3E4-E5	7.9E-5	1.61E-6
E5-2E5	1.0E-4	2.3E-6
2E5-3E5	1.0E-4	2.4E-6
3E5-E6	6.7E-5	1.6E-6

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Table 3Primary G-values for γ - and β -radiation

H ₂	H	E ⁻	H ₂ O ₂	OH	HO ₂	H ⁺	OH ⁻	-H ₂ O
0.45	0.55	2.66	0.72	2.67	0	2.76	0.1	6.87

Table 4

Radiolysis of water with mixed alpha and beta-radiation. Production of hydrogen from the cylindrical surfaces of all fuel pellets in one canister, i e in 4.3 l H₂O (144 m², thickness 30 μ m)

Storage time, y	Production, mol/y	
	Pure water	Fe ²⁺ solutions
40	4.9	1.04
100	3.6	0.91
300	2.5	0.70
1000	1.17	0.39
10 ⁴	0.25	0.096
10 ⁵	0.0130	0.0048
10 ⁶	0.0060	0.0020

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Table 5

β -radiolysis of pure water inside the cladding including the effect of α -radiolysis of the thin water film.

Storage time y	total G(H ₂)	Case 1A Diff in water			Case 1B Diff in bentonite			IP(H ₂) from ref 1 mol
		C(H ₂) at Equilib μM	$\frac{dP(H_2)}{dt}$ mol/y	IP(H ₂)* mol	C(H ₂) at Equilib μM	$\frac{dP(H_2)}{dt}$ mmol/y	IP(H ₂) mol	
40	1.95	167	0.89	0	51	0.40	0	0
100	2.05	162	0.87	53	57	0.44	0.03	260
300	2.15	135	0.72	210	60	0.47	0.12	860
E3	2.15	58	0.31	570	48	0.37	0.40	2100
E4	2.15	18	0.097	2400	22	0.170	2.8	8600
E5	2.79	1.57	8.4E-3	7100	217	1.70	87	21000
E6	2.49	0.74	3.9E-3	12600	35	0.25	970	29000

* Integrated Production

Table 6

γ -radiolysis of pure water outside the canister including the effect of α -radiolysis of the thin water film.

Storage time y	total G(H ₂)	Case 1C 1 cm canister			total G(H ₂)	Case 1D 10 cm canister			IP(H ₂) from refl mol
		C(H ₂) at Equilib M	$\frac{dP(H_2)}{dt}$ mol/y	IP(H ₂) mol		C(H ₂) at equilib M	$\frac{dP(H_2)}{dt}$ mol/y	IP(H ₂) mol	
40	3.78	0.154	1.20	0	1.03E3	0.58	4.53	0	0
100	24.0	0.42	3.25	130	8.28E3	0.46	3.61	240	260
300	1063	0.32	2.53	710	2.42E5	0.33	2.56	860	860
E3	1528	0.153	1.20	2000	3.21E5	0.5	1.17	2170	2100
E4	386	0.032	0.25	8500	3.54E4	0.032	0.25	8600	8600
E5	24.9	0.0017	0.013	20300	1.05E3	1.67E-3	0.013	20400	21000
E6	15.7	8.0E-4	6.3E-3	29000	6.38E2	7.8E-4	6.1E-3	29000	29000

* Integrated Production

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Table 7

β -radiolysis of Fe^{2+} solutions inside the cladding including the effect of α -radiolysis of the thin water film.

Storage time y	Total $G(\text{H}_2)$	Case 2A. Diff in water			Case 2B Diff in bentonite			IP(H_2) from ref 1 mol
		$C(\text{H}_2)$ at Equilibr	$\frac{dP(\text{H}_2)}{dt}$ mol/y	IP(H_2)* mol	$C(\text{H}_2)$ at Equilibr	$\frac{dP(\text{H}_2)}{dt}$ mmol/y	IP(H_2) mol	
		μM			mM			
40	0.77	330	1.80	0	1.33	10.4	0	0
100	0.85	280	1.53	100	1.51	11.8	0.7	58
300	0.93	220	1.19	370	1.72	13.5	3.2	220
E3	1.02	10.8	0.59	990	1.96	15.3	13.3	600
E4	1.10	3.4	0.185	4500	1.85	14.5	147	2800
E5	1.28	1.56	8.6E-3	13200	0.52	4.0	980	6900
E6	1.13	0.78	4.3E-3	19000	0.32	2.5	3900	9800

* IP = Integrated Production

Table 8

γ -radiolysis of Fe^{2+} solutions outside the canister including the effect of α -radiolysis of the thin water film.

Storage time y	Total $G(\text{H}_2)$	Case 2C 1 cm canister			Case 2D 10 cm canister				IP(H_2) from ref 1 mol
		$C(\text{H}_2)$ at Equilibr	$\frac{dP(\text{H}_2)}{dt}$ mol/y	IP(H_2) mol	Total $G(\text{H}_2)$	$C(\text{H}_2)$ at Equilibr	$\frac{dP(\text{H}_2)}{dt}$ mol/y	IP(H_2) mol	
		mM				M			
40	1.16	2.6	0.020	0	218	0.108	0.85	0	0
100	6.4	38	0.29	9	2.09E3	0.115	0.90	53	58
300	298	82	0.64	100	6.76E4	0.091	0.71	210	220
E3	510	48	0.37	480	1.07E4	0.050	0.39	600	600
E4	148	10.6	0.083	2500	1.36E4	0.012	0.095	2800	2800
E5	9.5	0.46	3.6E-3	6400	388	6.1E-4	4.8E-3	7300	6900
E6	5.5	0.22	1.7E-3	8800	213	2.6E-4	2.0E-3	10300	9800

Table 9

γ -radiolysis of Fe^{2+} solutions inside the cladding including the effect of α -radiolysis of the thin water film. Only H_2 diffuses out of the α -irradiated layer.

Storage time	Total $G(\text{H}_2)$	Case 3A. Diff in water				Case 3B. Diff in bentonite				IP(H_2) from ref 1 mol
		C(H_2) at Equilibr	$\frac{dP(\text{H}_2)}{dt}$	IP(H_2)*	IP(H_2) from case 2A	C(H_2) at Equilibr	$\frac{dP(\text{H}_2)}{dt}$	IP(H_2)	IP(H_2) from case 2B	
Y		μM	mol/y	mol	mol	mM	mmol/y	mol	mol	mol
40	0.77	383	2.10	0	0	2.1	16.9	0	0	0
100	0.85	319	1.75	120	100	2.9	23.0	1	1	58
300	0.93	258	1.41	1430	370	4.1	31.8	7	3	220
E3	1.02	127	0.70	1170	990	5.2	41.1	32	13	600
E4	1.10	39	0.21	5300	4500	4.1	32.0	360	150	2800
E5	1.28	1.75	9.6E-3	15100	1320	0.67	5.31	2040	980	6900
E6	1.13	0.85	4.7E-3	21600	19000	0.39	3.07	5800	3900	9800

* Integrated production

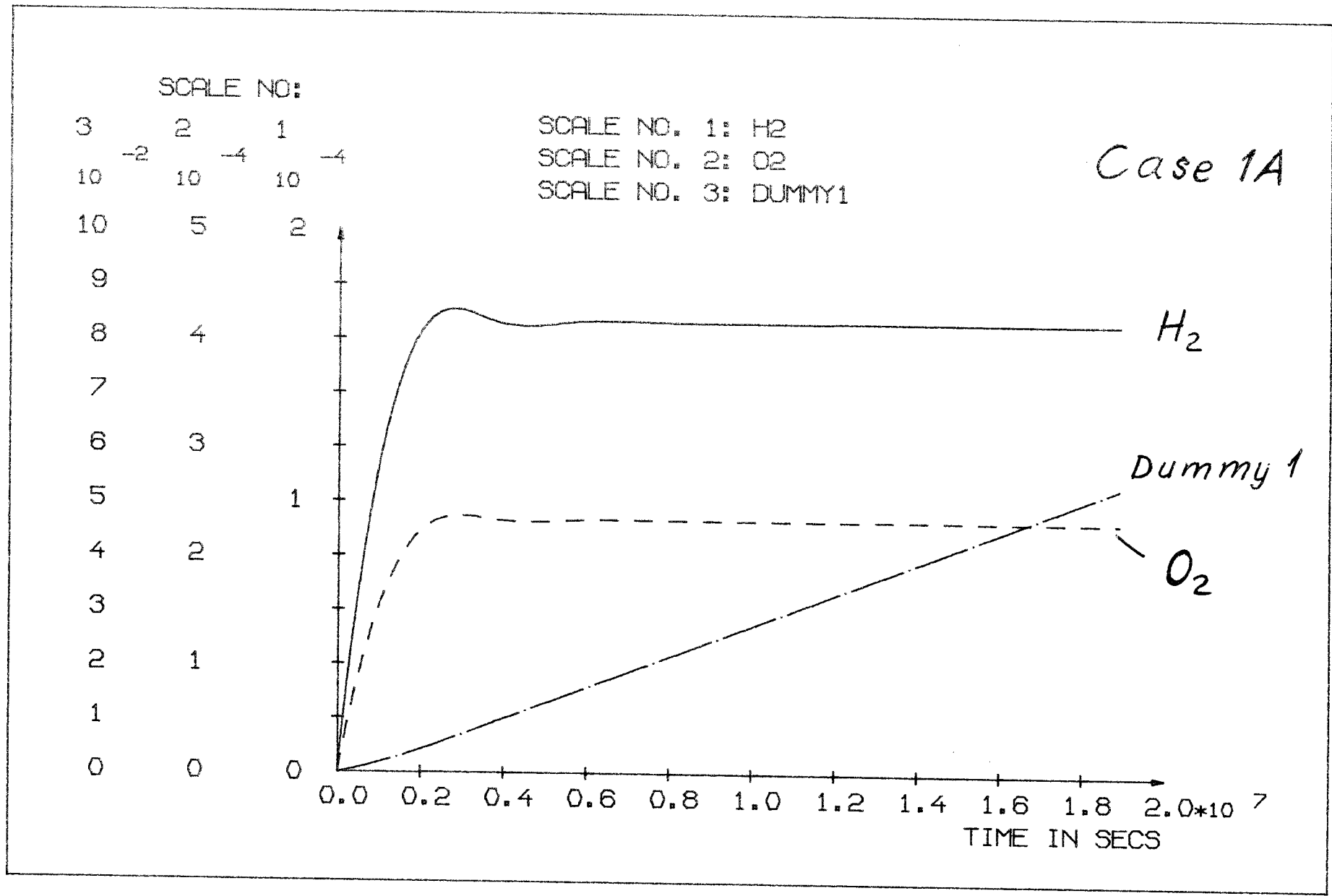


Figure 1

Case 1A. β -irradiation of pure water inside the fuel cladding. Diffusion in water. Storage time 40 y. Dummy 1 represents H₂ diffused out of the system. Molar units.

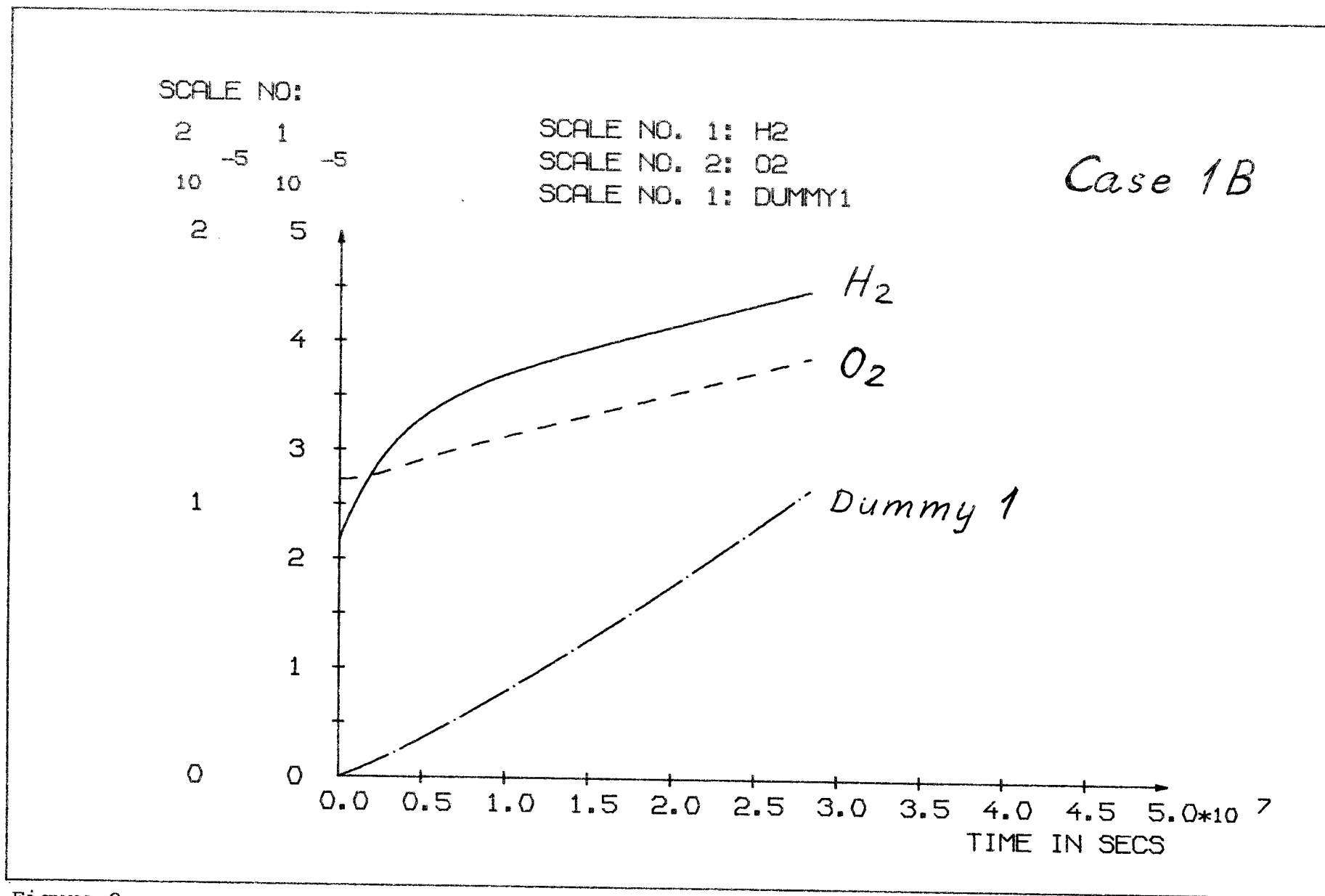


Figure 2a

Case 1B, first part. β -irradiation of pure water inside the fuel cladding. Diffusion in bentonite. Storage time 100.000 y. Dummy 1 represents H₂ diffused out of the system. Molar units.

Case 1B

SCALE NO:

3	2	1
-3	-4	-4
10	10	10
5	2	5

SCALE NO. 1: H₂
SCALE NO. 2: O₂
SCALE NO. 3: DUMMY1

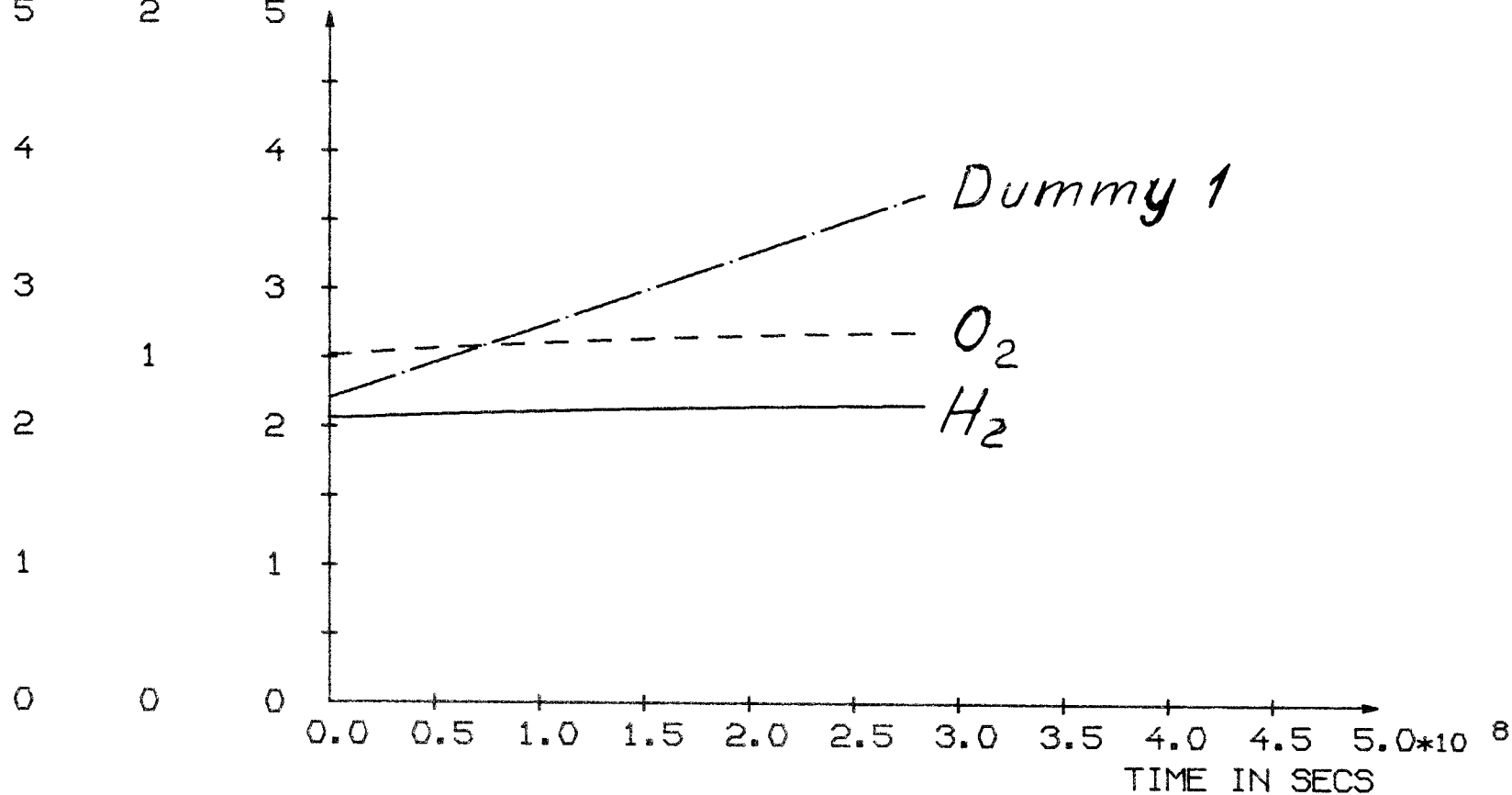


Figure 2b

Case 1B, last part (starting 6.8×10^8 s after the first part). β -irradiation of pure water inside the fuel cladding. Diffusion in bentonite. Storage time 100.000 y. Dummy 1 represents H₂ diffused out of the system. Molar units.

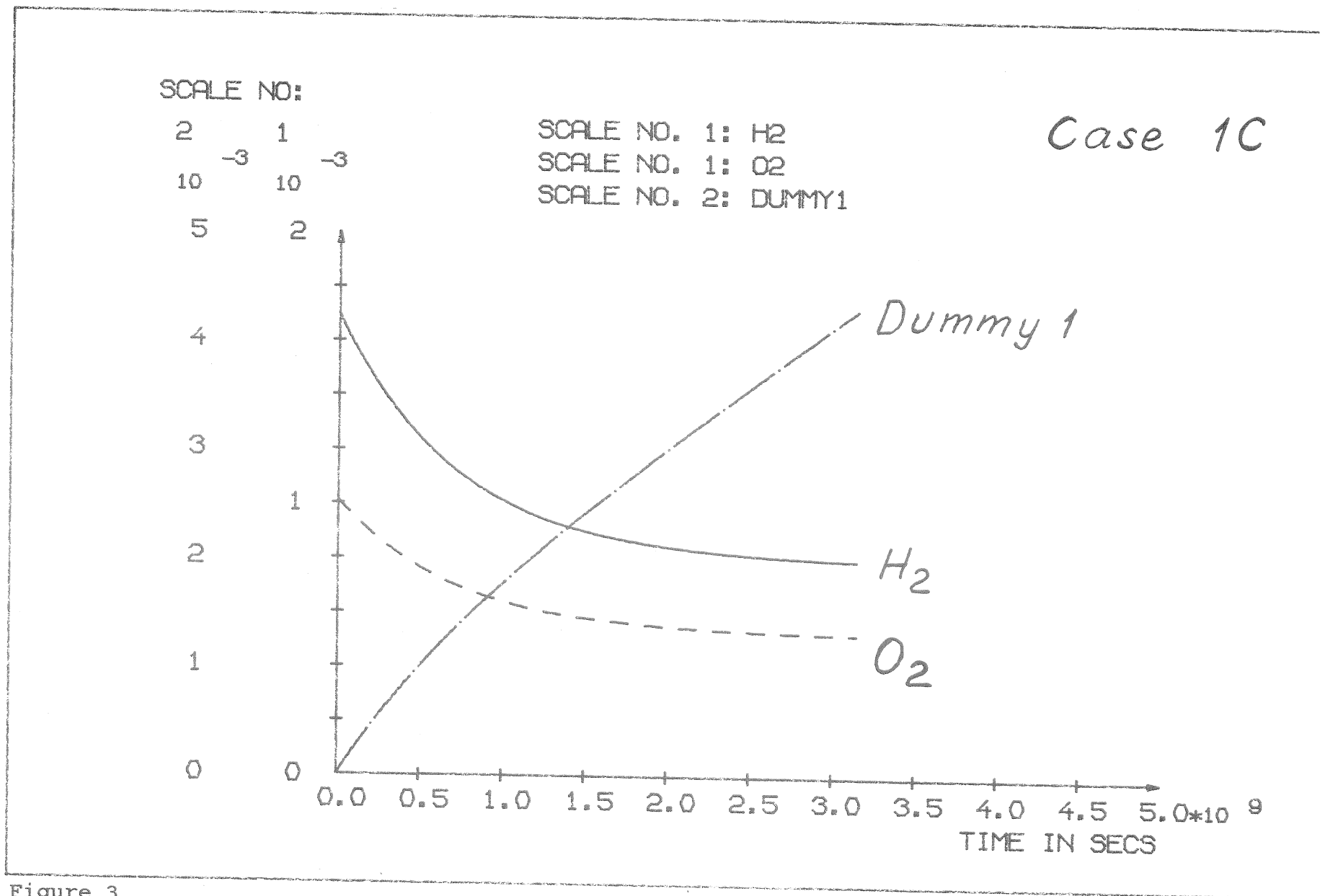


Figure 3

Case 1C. γ -irradiation of pure water outside the canister. Canister thickness 1 cm. Dummy 1 represents H₂ diffused out of the system. Molar units.

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1977-78

TR 121

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TR 79-28

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1984

TR 84-01

Radionuclide transport in a single fissure

A laboratory study of Am, Np and Tc

Trygve E Eriksen

Royal Institute of Technology

Stockholm, Sweden 1984-01-20

TR 84-02

Radiolysis of concrete

Hilbert Christensen

Studsvik Energiteknik AB,

Nyköping, Sweden

Erling Bjergbakke

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