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Radiolysis of groundwater from HLW stored in copper canisters

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Studsvik Energiteknik AB, 1982-06-29

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ERRATA

H Christensen and E Bjergbakke: Radiolysis of ground water from HLW stored in copper canisters, SKBF/KBS TR 82-02 (1982.

Please correct a misprint on p 22, Table 7, table heading

Reads: Hydrogen concentration in the gas phase, mM

Should read: Hydrogen concentration in the gas phase, µM.

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Studsvik **Report**

STUDSVIK/NW–82/273

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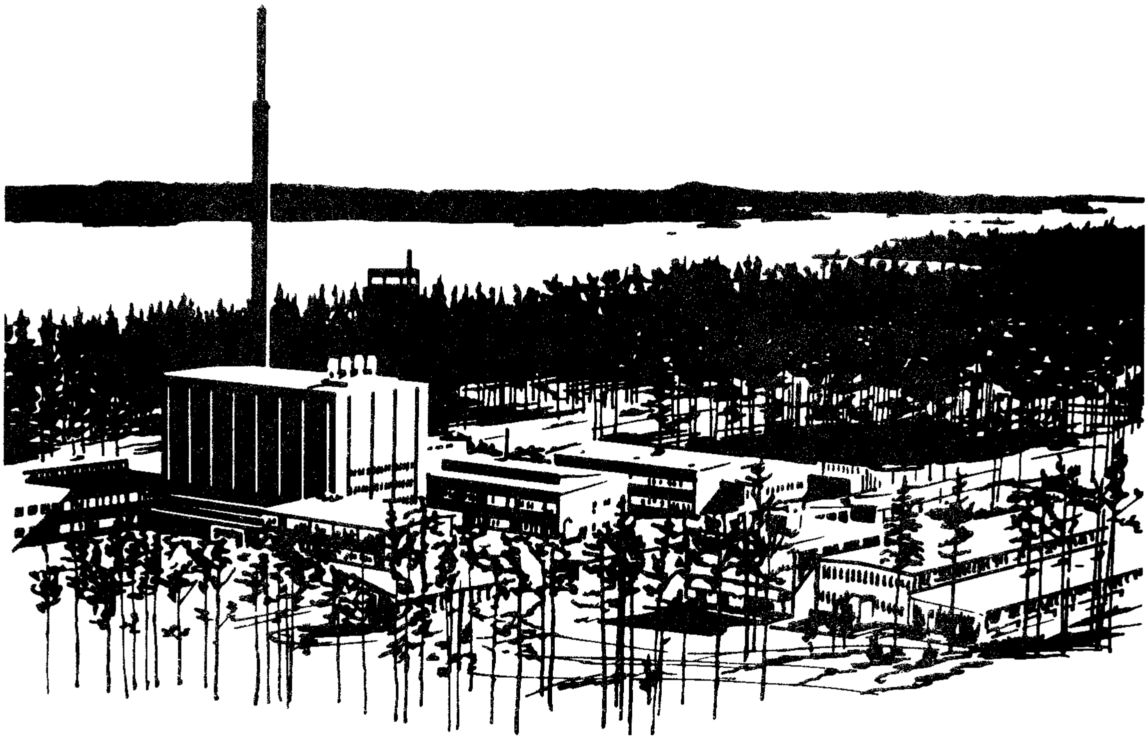

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STUDSVIK/NW-82/273

1982-06-29

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Swedish Nuclear Fuel Safety
Project

RADIOLYSIS OF GROUNDWATER FROM HLW STORED IN COPPER CANISTERS

A large number of computer calculations of the radiolysis of ground water outside copper canisters have been carried out.

At dose rates higher than 5×10^{-2} rad/s the hydrogen concentration is constant, approximately 10^{-3} mol/dm^3, and independent of time and dose rate. Therefore the rate of diffusion out of the system is constant, approximately 7×10^{-4} mol/year. At dose rates lower than 5×10^{-4} rad/s the logarithm of the hydrogen production is proportional to the logarithm of the dose rate. The hydrogen production depends on fuel type, burn-up and canister thickness only to the extent that the dose rate varies with these parameters.

The hydrogen production is independent of the volume of water in which the energy is assumed to be absorbed (5 or 15 cm layers outside the surface of the canister).

The hydrogen production depends on the concentration of Fe^{2+} ions in the water. In the basic calculations the concentration was assumed to be 5 ppm. An increase to 50 ppm increases the total hydrogen production after one million years outside a 1 cm thick canister from 360 to 1000 mol. A decrease to 0.5 ppm decreases the same yield to 80 mol.

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1. INTRODUCTION

According to a proposal by I Neretnieks and co-workers (1) an excess of oxidizing radicals from radiolysis of ground water ("oxrad") may cause a migrating front of radioactive nuclides. Some nuclides become more soluble after oxidation, but will precipitate again after having diffused a distance due to reduction by Fe^{2+} ions. Molecular hydrogen is formed as a primary product in the radiolysis of water and - being rather inactive - may be responsible for the excess of the oxidizing radicals.

We have made calculations of the radiolysis of ground water outside the canister, assuming varying wall thicknesses, and various iron contents in the water. Iron is assumed to be leached from the bentonite, so that a constant concentration is kept in the water phase.

Initial estimations were made assuming a constant G-value of hydrogen of 0.45 and neglecting recombination reactions. In the next step computer calculations were carried out in which recombination reactions, and reactions simulating the diffusion of hydrogen and oxygen could be included. Calculations were carried out for up to 1 million years.

Calculations were carried out for HLW waste with different origin. The matrix of interest for Swedish HLW waste is given in Table 1. Calculations were carried out for all the framed points in the matrix.

2. EXPERIMENTAL CONDITIONS

2.1 Yields of primary radiolysis products

The G-value for hydrogen production depends on the LET of the radiation (LET=Linear Energy Transfer). Under certain conditions, especially for the heavyer canister thicknesses, a substantial contribution of fast neutron radiation to the absorbed dose is experienced. Primary G-values for various types of radiation are given in Table 2. The values for neutrons are taken from ref 2.

2.2 Irradiation dose

The dose rates used were based on calculations carried out by Klas Lundgren (3). From his values of integrated energies absorbed in the water phase outside the canister at different times dose rates were calculated. We have "concentrated" the energies absorbed in an infinite volume into small volumes surrounding the surface of the canister. We have made calculations for two cases, 180 l water corresponding to a 5 cm bentonite/water layer, and 720 l water corresponding to a 15 cm layer.

Calculated doses, dose rates and neutron contributions at various times and for different waste types are given in Tables 3-5. Based on previous experience the doses have been increased with 30% due to energy transer from bentonite to the water phase. The dose rates given in Tables 3-5. corresponds to absorption in 180 l water. Corresponding values in 720 l water are 4 times lower.

2.3 Computer program

We have used a program developed by Lang-Rasmusen, Risö, Denmark. The program is based on DIFSUB (4). In principle the program translates the chemical equations of the complete reaction system into a set of differential equations, which is solved by numerical integration after specifications of rate constants, initial concentrations, G-values, irradiation dose and duration. The results are presented in tables giving the concentrations of the various species at various times during, and even after, the irradiation (if wanted). As an option the results may also be presented as curves showing the concentrations as a function of time.

As input data the program requires

a) a list of all chemical reactions,
b) rate constants for these reactions,
c) G-values for all the primary products,
d) initial concentrations of all species at the start of irradiation,
e) dose and duration of the irradiation.

a) and b) are given in Table 6.

The prediction power of the program has been tested by comparing calculations carried out using it with results measured by T Eriksen and J Lind (5). Eriksen and Lind irradiated bentonite-/water mixtures to various doses and mesured the hydrogen production in the gas phase. The correlation between measured and calculated results was very good, see Table 7. Calculated results have also been compared with literature data. In this case the correlation was also very good (6).

2.4 Iron ions

Fe^{2+} ions play an important role in the mechanism and affect the radiolysis. To obtain realistic results it is necessary to include radiolytic reactions of Fe^{2+} in the reaction scheme. Bentonite may contain up to 3% iron, calculated as Fe_2O_3, but in the reduced form (Fe^{2+}) (7). At present it is not known with certainty to which degree and at which rate this is dissolvable. If we assume about 1% to be dissolvable, 330 mole of Fe^{2+} may leach into the irradiated water content of the bentonite layer (720 l). We assume further that the leach rate is such that the Fe^{2+} concentration remains constant at 5 ppm (8.9×10^{-5}M). In a few additional calculations the concentrations was assumed to be either 8.9×10^{-4} M or 8.9×10^{-6} M. Fe^{3+} is assumed to precipitate at concentrations greater than 10^{-5}M.

2.5 Diffusion of hydrogen

Originally it was thought that the yield of oxrad could be calculated as the yield of hydrogen. It was therefore necessary to include an equation for the diffusion of hydrogen out of the system. This was done based on an equation taken from (7)

$$P = \frac{6.83 \times 10 \times N}{4\Pi \times r_1 \times C_{TOT} \times D_{eff}} \qquad \text{Eq 1}$$

where P = hydrogen pressure in bar
r_1 = 1 m (radius of waste canister, simplified as a sphere
D_{eff} = 2×10^{-11} m^2/s (coefficient of diffusion)
C_{TOT} = 55.6 $kmol/m^3$
N = production rate of hydrogen kmol/year

and Henry's law: $p=H\cdot X$, which may be written as

$$C = \frac{P \times 1000 \times \rho\ (H_2O)}{H \times 18} = P \times 7.82 \times 10^{-4}\ \mathrm{M} \qquad \text{Eq 2}$$

$$C = P \times 7.82 \times 10^{-4}\ \mathrm{M}\ (\text{at } 25^{\circ}\mathrm{C})$$

where H = Henry's constant, X is the mole fraction, ρ is the density, C is the concentration.

The radiation is assumed to be absorbed in a bentonite layer containing a water volume of 720 l outside of the canister, assuming a water-content of 0.45 ton/m^3. Equation 1 may therefore be rewritten as

$$-\frac{dC(H_2)}{dt} = N_D = P \times 2.7 \times 10^{-13} \qquad \text{Eq 3}$$

where $-\frac{dc(H_2)}{dt} = (N_D)$ is the hydrogen which disappears out of the system by diffusion (expressed as $M\cdot s^{-1}$). A combination of Equations 2 and 3 gives Equation 4.

$$N_D = C \times 3.46 \times 10^{-10}\ (M\cdot s^{-1}) \qquad \text{Eq 4}$$

Energy transfer from bentonite to water was included by increasing the calculated doses by a factor of 1.3. This has previously been shown to give a good correlation between experimental and calculated results, see Table 7.

3. RESULTS

3.1 Initial estimates

The results are shown in Table 8. The amount of hydrogen produced outside a 20 cm thick copper canister is negligible. The doses outside a 1 cm canister were estimated to be 10^5 times larger than outside a 20 cm canister.

3.2 Computer calculations

Some difficulties showed up in computer calculations extended over such long irradiation times as required for the present problem. It turned out to be necessary to reduce the equation system in Table 6. This was done by decreasing the rate constants of reactions establishing equilibriums (RE 10,11,19,20,26 and 27). The actual rate constants used in the calculations are those given in Table 6. (In some calculations the rates were reduced less.) But in all cases the equilibrium constants were kept at their original values.

3.2.1 Calculations in the absence of iron

A calculation in pure water was carried out for a dose rate of 2.7×10^{-6} rad/s corresponding to a canister thickness of 20 cm. The irradiation time was extended to 5000 years, when the amount of hydrogen produced (Dummy) was 2×10^{-3} mol. The integrated dose, 4.1×10^{5} rad, corresponds to a storage time of 3.7×10^{5} years. Detailed calculations were not carried out in this case as the conservative calculations showed that the effect of radiolysis was neglible. G-values for production of hydrogen and diffused hydrogen ($=N_D$) were calculated and are shown in Table 9.

Initially, the dose rate outside a 1 cm thick copper canister was estimated to be 0.27 rad/s. Calculations with this dose rate in pure water were extended to 60 years. G-values for both hydrogen and N_D (=hydrogen diffused away) are low, see Table 9. The yields increase after longer irradiation times (300 y, see Table 9), but decrease if oxygen is also allowed to diffuse away. The yields are very low in all the calculated examples, but appear to increase with time.

3.2.2 Calculations in the presence of iron ions

In order to obtain more realistic results, we introduced iron and the necessary chemical equations into the system. This turned out to "stabilize" the computer calculations.

In the basic calculations the Fe^{2+} concentration in water was kept constant at 5 ppm (8.9×10^{-5} M). Later on calculations with other concentrations were carried out. The results are presented in Figures 1 and 2 corresponding to absorption in 180 and 720 l water, respectively (5 ppm Fe^{2+}). The hydrogen production corresponds to the hydrogen diffused out of the system. The hydrogen production is independent of dose rate at dose rates higher than 5×10^{-2} rad/s. In this case the hydrogen concentration in the water obtains an equilibrium value of 10^{-3} M. The concentration depends on the Fe^{2+} concentrations due to the two competing reactions, 14 and 29.

$$OH + H_2 \rightarrow H + H_2O \qquad (14)$$

$$H^+ + OH + Fe^{2+} \rightarrow Fe^{3+} + H_2O \qquad (29)$$

which keep $C(H_2)$ almost constant independent of dose rate.

At lower dose rates (<5×10^{-4} rad/s) the logarithm of the hydrogen production is proportional to the logarithm of the dose rate corresponding to an almost constant G-value of 0.9.

This latter part of the curve is higher for the 720 l water case compared with the 180 l case, the rates being 4 times higher. The part with constant rate (dose rate >5×10^{-2} rad/s) is placed at the same level in the two cases.

Points for conditions with a substantial contribution of fast neutrons to the dose are placed a little above the curve. This is because irradiation with fast neutrons gives a higher primary yield of hydrogen. Points corresponding to initial conditions (storage time 40-60 y) are placed a little below the curve. The reason is that hydrogen has not yet attained its equilibrium value for the given dose rate.

For each dose rate the hydrogen concentration attains an equilibrium value after a certain time, see Figure 3. The integrated hydrogen production and the production rate are shown as a function of time in Figure 4 for a copper thickness of 1 cm and in Figure 5 for a thickness of 20 cm. In Table 10 the total hydrogen productions are given for various waste conditions. The yields are the same for the 180 and 720 l case.

If 1% of the iron content of the bentonite can be leached into the water, 330 Mol of Fe^{2+} is accessible in the case with 720 l H_2O. Oxidation of these 330 Mol corresponds to a hydrogen production of 165 Mol, somewhat less than the hydrogen produced after one million years in the worst case. However, during this time iron from other areas may be transported into the reaction zone. It is very likely that actinides will be protected from oxidation by the presence of Fe^{2+} ions.

The total hydrogen production after one million years, ca 400 mol for the thinnest copper canister, is considerably lower than the previously conservatively estimated value of 23 000 mol. The main reason for this difference is the difference in dose rates used in the two cases. It was previously estimated that the dose rate increased with a factor of 10^5 when the canister thickness was reduced from 20 cm to 1 cm. Detailed calculations (3) have shown, however, that this is not the case, see Table 11, which shows that the dose rate ratio varies considerably with storage time.

Change of diffusion coefficient

In one calculation the diffusion coefficient of hydrogen was increased with a factor of 10 from 2×10^{-11} m^2/s to 2×10^{-10} m^2/s. Results for calculations with these two diffusion coefficients can be compared in Table 12 for PWR 45, 10 cm. During the first 600 years the production is higher using the high diffusion rate; after 600 years the rates are equal and the total productions after one million years are 9.4 and 9.5 mol, respectively.

Change of iron concentration

Fe^{2+} ions have a dominating effect on the radiolysis of water. We have, therefore, made calculations with water containing 10 times less or 10 times more Fe^{2+} ions than used in the basic calculations, in which the concentration of Fe^{2+} ions was kept at 8.9×10^{-5} M (=5ppm). The results of calculations, assuming energy absorption in 720 l water, can be seen in Figure 6. For comparison the results of the initial estimates and of the basic calculations (water with 8.9×10^{-5} M Fe^{2+} ions) are included. The effects of the change in iron concentration are large at the plateau level, the plateau lying at 1.1, 8×10^{-3}, and 1.4×10^{-4} mol/year for Fe^{2+} concentrations of 8.9×10^{-4}, 8.9×10^{-5} and 8.9×10^{-6} M, respectively. The competition between reaction 14 and 29 does no longer play an important role for the determination of the hydrogen equilibrium concentration. Instead, the equilibrium is determined by the formation through reactions 30,31 and 33 and the primary reaction

$$H_2O \rightsquigarrow H_2,\ H_2O_2,\ H,\ e^-_{aq},\ OH$$

and removal through reactions 14 and 28 (diffusion reaction). In table 13 some of the important reactions are shown togehter with rate constants and the relevant concentrations. It can be seen that it is only in the basic calculations (i.e. calculations with $Fe^{2+} = 8.9 \times 10^{-5}$ M) that competition between reactions 14 and 29 determines the equilibrium level of hydrogen. The straight lines in Figure 6 corresponds to nearly constant G-values of 2.0 and 0.5 for iron concentration of 8.9×10^{-4} and 8.9×10^{-6} M, respectively. This may be compared with the results of the basic calculations, in which the G-value was 0.9. The effect of iron concentration on the total hydrogen production can be seen in table 14. Outside a 1 cm canister the total hydrogen production was increased after one million years from 360 to 1000 mol when the iron concentration was increased from 8.9×10^{-5} to 8.9×10^{-4} M.

4. CONCLUSIONS

At dose rates higher than $5x10^{-2}$ rad/s the hydrogen concentration is constant, approximately 10^{-3} mol/dm^3, and independent of time and dose rate. Therefore the rate of diffusion out of the system is constant, approximately $7x10^{-4}$ mol/year. At dose rates lower than $5x10^{-4}$ rad/s the logarithm of the hydrogen production is proportional to the logarithm of the dose rate. The hydrogen production depends on fuel type, burn-up and canister thickness only to the extent that the dose rate varies with these parameters.

The hydrogen production is independent of the volume of water in which the energy is assumed to be absorbed (5 or 15 cm layers outside the surface of the canister).

The hydrogen production depends on the concentration of Fe^{2+} ions in the water. In the basic calculations the concentration was assumed to be 5 ppm. An increase to 50 ppm increases the total hydrogen production after one million years outside a 1 cm thick canister from 360 to 1000 mol. A decrease to 0.5 ppm decreases the same yield to 80 mol.

The yield of hydrogen may also represent an upper limit for the corrosion which radiolysis of ground water surrounding the canister can cause.

Acknowledgement

The valuable assistance of Ole Lang Rasmussen in computer programming is gratefully acknowledged.

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TABLE 1. Waste matrix

		Lead-filled canister of thickness, mm				HIP* canister of thickness, mm			
Fuel type	Burn-up MWd/t	200	100	60	10	200	100	60	10
	45	X	X	X	X	X	X	X	X
PWR	38	X	X	X	X	X	X	X	X
	33	X	X	X	X	X	X	X	X
	38	X	X	X	X	X	X	X	X
BWR	33	X	X	X	X	X	X	X	X
	28	X	X	X	X	X	X	X	X

Manufactured by Hot Isostatic Pressing of copper powder.

TABLE 2. Primary G-values for gamma-radiation with varying contributions of fast neutrons to the dose.

Contribution of neutrons, gamma		G-values								
%	%	H_2	H	E^-	H_2O_2	OH	HO_2	H^+	OH^-	$-H_2O$
0	100	0.45	0.44	2.8	0.72	2.7	0	2.9	0.1	7.04
10	90	0.52	0.43	2.56	0.745	2.48	0.02	2.65	0.09	6.66
20	80	0.58	0.42	2.31	0.775	2.25	0.03	2.39	0.08	6.25
30	70	0.65	0.41	2.07	0.805	2.02	0.05	2.14	0.07	5.87
40	60	0.72	0.41	1.83	0.835	1.80	0.07	1.89	0.06	5.50
100	0	1.12	0.36	0.36	1.00	0.47	0.17	0.36	0	4.00

TABLE 3. Doses and dose rates absorbed in 180 l water.

	PWR 33, 10 cm			PWR 38, 10 cm			PWR 45, 10 cm		
Time,year	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons %	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons %	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons %
40-60	5.86E5	9.3E-4	0	6.74E5	1.07E-3	0	8.06E5	1.28E-3	0
60-100	5.54E5	4.4E-4	0	6.24E5	4.95E-4	0	7.42E5	5.89E-4	0
100-300	3.59E5	5.7E-5	1	4.16E5	6.60E-5	0	4.92E5	7.81E-5	0
300-600	9.88E3	1.04E-6	30	1.80E4	1.89E-6	10	2.77E4	2.92E-6	20
600-E3	1.05E4	8.3E-7	30	1.08E4	8.60E-7	30	2.12E4	1.68E-6	30
E3-3E3	3.02E4	4.8E-7	30	4.23E4	6.71E-7	30	6.93E4	1.10E-6	40
3E3-E4	9.24E4	4.2E-7	20	1.16E5	5.28E-7	30	1.92E5	8.73E-7	30
E4-3E4	3.65E5	5.8E-7	10	4.49E5	7.13E-7	10	5.86E5	9.30E-7	10
3E4-E5	2.64E6	1.2E-6	10	2.84E6	1.29E-6	10	3.63E6	1.65E-6	10
E5-2E5	5.44E6	1.7E-6	0	6.37E6	1.99E-6	0	7.52E6	2.35E-6	0
2E5-3E5	6.72E6	2.1E-6	0	6.66E6	2.08E-6	0	8.29E6	2.59E-6	0
3E5-E6	2.64E7	1.2E-6	0	2.97E7	1.35E-6	5	3.54E7	1.61E-6	6

Explanations: PWR 33 is PWR fuel with a burn-up of 33 MWd/ton. 10 cm is the canister thickness.

TABLE 4. Doses and dose rates absorbed in 180 l water.

	PWR 38, 6 cm HIP			BWR 33, 6 cm, HIP			BWR 33, 1 cm		
Time,year	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons,%	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons,%	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons,%
40-60	4.92E6	7.81E-3	0	8.57E6	1.36E-2	0	2.33E8	0.37	0
60-100	4.84E6	3.84E-3	0	8.38E6	6.65E-3	0	2.40E8	0.19	0
100-300	3.25E6	5.16E-4	0	5.63E6	8.94E-4	0	1.64E8	2.6E-2	0
300-600	7.36E4	7.75E-6	0	2.20E5	2.31E-5	0	6.46E6	6.8E-4	0.2
600-E3	7.37E4	5.85E-6	0	7.52E4	5.97E-6	0	2.14E6	1.7E-4	0.3
E3-3E3	7.81E4	1.24E-6	7	1.55E5	2.46E-6	6	6.93E6	1.1E-4	0.5
3E3-E4	2.29E5	1.04E-6	6	4.58E5	2.08E-6	6	3.3E7	1.5E-4	0.3
E4-3E4	1.10E6	1.75E-6	0	1.29E6	2.05E-6	0	9.45E7	1.5E-4	0.2
3E4-E5	6.05E6	2.75E-6	0	1.25E7	5.67E-6	0	1.74E8	7.9E-5	0.3
E5-2E5	1.54E7	4.82E-6	0	2.61E7	8.17E-6	0	3.2E8	1.0E-4	0.3
2E5-3E5	2.24E7	6.99E-6	0	2.76E7	8.63E-6	0	3.2E8	1.0E-4	0.3
3E5-E6	6.53E7	2.97E-6	0	1.21E	5.52E-6	0	1.47E9	6.7E-5	0.4

Explanations: BWR 33 is BWR fuel with a burn-up of 33 MWd/ton. 1 cm is the canister thickness. HIP refers to a canister made by hot isostatic pressing.

TABLE 5. Doses and dose rates absorbed in 180 l water.

	BWR 33, 10 cm			BWR 33, 20 cm		
Time,year	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons,%	Integrated dose, rad	Dose rate rad/s	Contribution of neutrons,%
40-60	8.25E5	1.31E-3	0	5.70E3	9.05E-6	20
60-100	7.03E5	5.58E-4	0	4.66E3	3.7E-6	20
100-300	4.67E5	7.41E-5	1	6.93E3	1.1E-6	30
300-600	2.53E4	2.66E-6	10	4.18E3	4.4E-7	30
600-E3	1.08E4	8.6E-7	30	4.16E3	3.3E-7	30
E3-3E3	4.28E4	6.8E-7	30	1.51E4	2.4E-7	30
3E3-E4	1.25E5	5.7E-7	30	3.52E4	1.6E-7	30
E4-3E4	5.04E5	8.0E-7	10	6.93E4	1.1E-7	30
3E4-E5	3.54E6	1.61E-6	5	2.42E5	1.1E-7	20
E5-2E5	7.36E6	2.3E-6	4	4.48E5	1.4E-7	20
2E5-3E5	7.68E6	2.4E-6	4	5.12E5	1.6E-7	20
3E5-E6	3.52E7	1.6E-6	3	2.20E6	1.0E-7	30

Explanations: BWR 33 is BWR fuel with a burn-up of 33 MWd/ton. 10 cm is the canister thickness.

TABLE 6. Reaction scheme.	Rate constant M^{-1} S^{-1}
RE1: $2E^- = 2\ OH^- + H_2$	5E9
RE2: $E^- + OH = OH^- + H_2O$	2E10
RE3: $2\ OH = H_2O_2$	4E9
RE4: $OH + O_2^- = O_2 + OH^-$	E10
RE5: $OH^- + H = E^-$	2E7
RE6: $E^- + H^+ = H + H_2O$	2.2E10
RE7: $E^- + H = OH^- + H_2$	2E10
RE8: $E^- + H_2O_2 = OH + OH^- + H_2O$	1.6E10
RE9: $E^- + H_2O = H + OH^- + H_2O$	2E1
RE10: $H^+ + OH^- = H_2O$	1.444E8
RE11: $H_2O = OH^- + H^+$	2.599E-8
RE12: $2\ H = H_2$	E10
RE13: $H + OH = H_2O$	2.5E10
RE14: $OH + H_2 = H + H_2O$	4E7
RE15: $OH + H_2O_2 = H_2O + HO_2$	2.25E7
RE16: $H + H_2O_2 = OH + H_2O$	6E7
RE17: $E^- + O_2 = O_2^- + H_2O$	2E10
RE18: $H + O_2 = HO_2$	2E10
RE19: $HO_2 = O_2^- + H^+$	8E1
RE20: $H^+ + O_2^- = HO_2$	5E6
RE21: $HO_2 + O_2^- = O_2 + HO_2^-$	8.5E7
RE22: $H + HO_2 = H_2O_2$	2E10
RE23: $H + O_2^- = HO_2^-$	2E10
RE24: $E^- + HO_2 = HO_2^- + H_2O$	2E10
RE25: $E^- + O_2^- = HO_2^- + OH^-$	1.3E10
RE26: $OH^- + H_2O_2 = HO_2^- + H_2O$	5E2
RE27: $H_2O + HO_2^- = H_2O_2 + OH^-$	5.735E-2
RE28: $H_2 =$ Dummy 1	3.46E-10

TABLE 6, continued. Addition in the presence of iron ions.

	Rate constant M^{-1} S^{-1}
RE29: $Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-$	3.4E8
RE30: $Fe^{2+} + E^- \rightarrow Fe^{3+} + OH^- + H^-$	1.2E8
RE31: $H^- + H_2O \rightarrow H_2 + OH^-$	E-2
Re32: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$	60
RE33: $Fe^{2+} + H \rightarrow Fe^{3+} + H^-$	1.3E7
RE34: $Fe^{2+} + O_2^- \rightarrow Fe^{3+} + O_2^{2-}$	4E8
RE35: $Fe^{3+} + E^- \rightarrow Fe^{2+} + H_2O$	2E10
RE36: $Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2$	4E8
RE37: $O_2^{2-} + H_2O \rightarrow HO_2^- + OH^-$	E-3
RE38: $Fe^{3+} + H \rightarrow Fe^{2+} + H^+$	E8
RE39: $A \rightarrow Fe^{2+}$	E-7
RE40: $Fe^{2+} \rightarrow A$	1.12E-2
RE41: $Fe^{3+} + OH^- \rightarrow FeOH$	E4
RE42: $FeOH \rightarrow Fe^{3+} + OH^-$	E-9

TABLE 7. Radiolysis of bentonite/water mixtures in the presence of a gas phase. Dose rate 156 rad/s. Comparison of measured and calculated results.

Water content in the bentonite, %		Dose** Mrad	Hydrogen concentration in the gas phase, mM	
During calculations	During* measurements		Measured	Calculated
3				7
4.5	0	1.4	4	9.5
6				12
14.5	10	2	23	26
31.5	27	1	28	28

*It has later been estimated that the dryed bentonite which in the experiments was assumed to contain 0% water actually contained 3-6% water.

**The dose in the measurement. Due to energy transfer from bentonite to water the dose used in the calculations are 30% higher.

TABLE 8. G-values, doses and hydrogen yields outside a copper canister.

Time year	Fraction of neu-trons %	$g(H_2)$	From neu-trons, γ, and total	Integrated dose 10^{17} MeV	Dose* rate 10^{-8} rad/s	Accumulated hydrogen, mol for thickness of canister, cm			
						20	10	6	1
	0	0,45							
	100	1.12							
	5	0.06	n		270				
		0,43	γ						
10^2		0,49	tot	1,8		0,0015	0,44	7,1	150
	40	0,45	n		25				
		0,27	γ						
10^3		0,72	tot	4,3		0,0051	1,50	24	510
	20	0,22	n		7				
		0,36	γ						
10^4		0,58	tot	11,2		0,0108	3,20	51	1 080
	10	0,11	n		2,5				
		0,41	γ						
10^5		0,52	tot	35		0,030	9,0	143	3 000
	2	0,02	n						
		0,44	γ		2,7				
10^6		0,46	tot	300		0,23	69,0	1100	23 000

*including energy transfer from bentonite. Valid for 20 cm copper. For 10,6 and 1 cm multiply by 300, 4800 and 10^5, respectively.

TABLE 9. G-values for the formation of hydrogen and N_d* in the absence of iron. Absorption in 720 l water.

Dose rate rad/s	$G(H_2)$	$G(N_D)$	Time	Comments
2.7×10^{-6}	6×10^{-4}	7×10^{-3}	5000 y	
2.7×10^{-1}	5.2×10^{-8}	3.8×10^{-8}	60 y	
2.7×10^{-1}	3.5×10^{-7}	0.71×10^{-7}	300 y	
2.7×10^{-1}	4.5×10^{-8}	3.3×10^{-8}	300 y	diffusion of oxygen included

* Hydrogen diffused out of the system

TABLE 10. Total hydrogen production in the presence of 5 ppm Fe^{2+} ions.

Fuel type	Burn-up MWd/t	Canister thickness, cm	Water volume, l	Production (mol H_2) after various storage times (year)					
				100	10^3	10^4	10^5	$3x10^5$	10^6
BWR	33	1	180	1	3	8	47	138	390
BWR	33 HIP	6	180	1	1	1	3	12	32
BWR	33	10	180	0.15	0.23	0.26	1	3	9
BWR	33	20	180	2E-3	5E-3	1E-2	7E-2	0.2	0.6
BWR	33	1	720	1	3	9	47	138	360
BWR	33 HIP	6	720	0.3	0.7	0.8	3	12	32
BWR	33	20	720	2E-3	5E-3	1.4E-2	7E-2	0.2	0.6
PWR	33	10	180	0.13	0.18	0.20	0.7	2.7	7
PWR	38	10	180	0.14	0.20	0.23	0.7	2.8	8
PWR	45	10	180	0.15	0.27	0.33	1.0	3.6	9
PWR	38 HIP*	6	180	0.4	0.7	0.8	2	8	19
PWR	38 DIFF**	10	180	0.23	0.32	0.36	1.1	3.6	9

*HIP: Manufactured by Hot Isostatic Pressing

**Diff: 10 times higher diffusion coefficient for hydrogen used.

TABLE 11. Comparison of dose rates using canisters with a copper thickness of 1 and 20 cm, see ref 3.

	Storage time,y	Dose rates, mGy/h					
		40	100	300	600	10^4	$3x10^5$
Canister thickness	1 cm	1.97E4	4730	67.1	14.1	2.05	3.51
	20 cm	0.131	1.98E-2	2.31E-3	1.68E-3	6.17E-4	1.15E-3
Dose rate ratio		$1.5x10^5$	$2.4x10^5$	$2.9x10^4$	$8.4x10^3$	$3.3x10^3$	$3.0x10^3$

TABLE 12. Comparison of hydrogen production using two different diffusion coefficients. PWR 45, 10 cm.

	Hydrogen production			
	Diff=$2x10^{-11}$ m^2/s		Diff=$2x10^{-10}$ m^2/s	
Time, year	$\frac{dH_2}{dt}$ mol/year	Integrated H_2-production mol	$\frac{dH_2}{dt}$ mol/year	Integrated H_2-production mol
40-60	2.3E-3	0.09	5.6E-3	0.11
60-100	1.9E-3	0.15	2.8E-3	0.23
100-300	3.6E-4	0.22	4.0E-3	0.31
300-600	1.5E-5	0.27	1.6E-5	0.31
600-1000	9.8E-6	0.28	9.8E-6	0.32
E5-2E5	1.2E-5	2.2	1.2xE-5	2.3
3E5-E6	8.4E-6	9.4	8.4xE-6	9.5

TABLE 13. Reactions, rate constants and concentrations of importance for determination of hydrogen equilibria.

	Reaction No	Rate Constant(K) $M^{-1}.s^{-1}$	Conc(c) M	k.c s^{-1}
$OH+H_2$ -> H	14	4E7	8.8E-2	3.5E6
$OH+Fe^{2+}$ -> Fe^{3+}	29	3.4E8	8.9E-4	3E5
$OH+H_2$ -> H	14	4E7	1.7E-5	6.9E2
$OH+Fe^{2+}$ -> Fe^{3+}	29	3.4E8	8.9E-6	3E3
$OH+H_2$ -> H	14	4E7	9E-4	3.6E4
$OH+Fe^{3+}$ -> Fe^{3+}	29	3.4E8	8.9E-5	3E4
H_2 -> Dummy	28	3.5E-10		
$e^-_{aq}+Fe^{3+}$ -> Fe^{2+}	35	2E10	E-5	2E5
e^-_{aq} + Fe^{2+} -> $Fe^{3+}+H^-$	30	1.2E8	8.9E-4	1.1E5
$H+Fe^{2+}$ -> $Fe^{3+}+H^-$	33	1.3E7	8.9E-4	1.2E4
$H+Fe^{3+}$ -> Fe^{2+}	38	E8	E-5	E3
H^-+H_2O -> H_2	31	E-2	55	0.6

TABLE 14. Total hydrogen production in 720 l groundwater outside a canister with BWR 33 fuel. Various iron concentrations.

Canister thickness	Fe^{2+} conc.	Production (mol H_2) after various storage times (year)				
cm	M	10^2	10^3	10^4	10^5	10^6
1	$8.9x10^{-4}$	140	140	160	260	1000
6	"	6	8	8	13	76
1	$8.9x10^{-5}$	1	3	8	47	360
6	"	1	1	1	3	32
1	$8.9x10^{-6}$	0.02	0.06	0.9	8	76
6	"	0.02	0.06	0.1	1.4	17

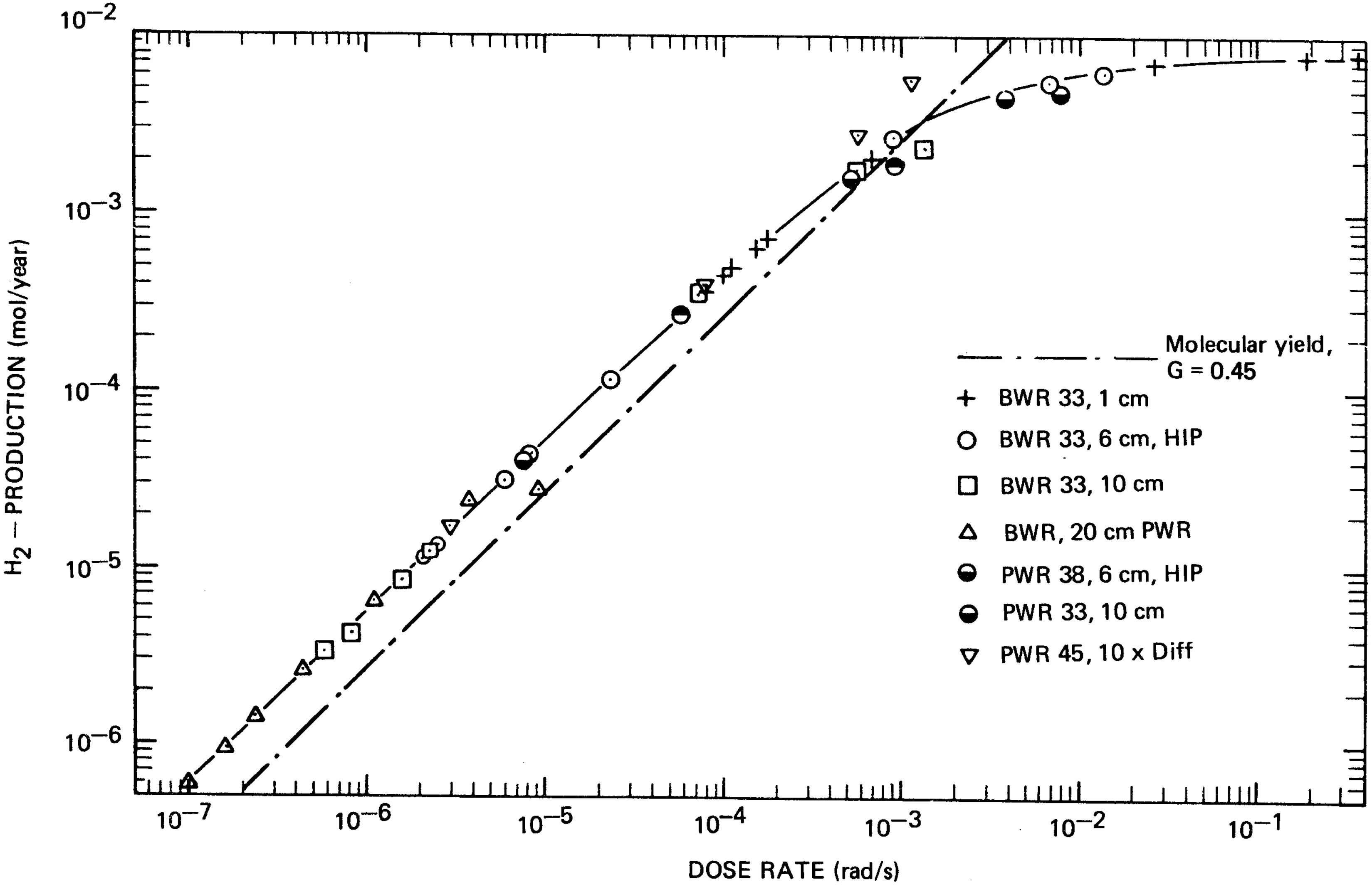

Figure 1. Hydrogen production as a function of dose rate. The radiation is absorbed in 180 l water. BWR 33, 1 cm means BWR fuel irradiated to 33 MWd/t, encapsulated in a copper canister with thickness of 1 cm.

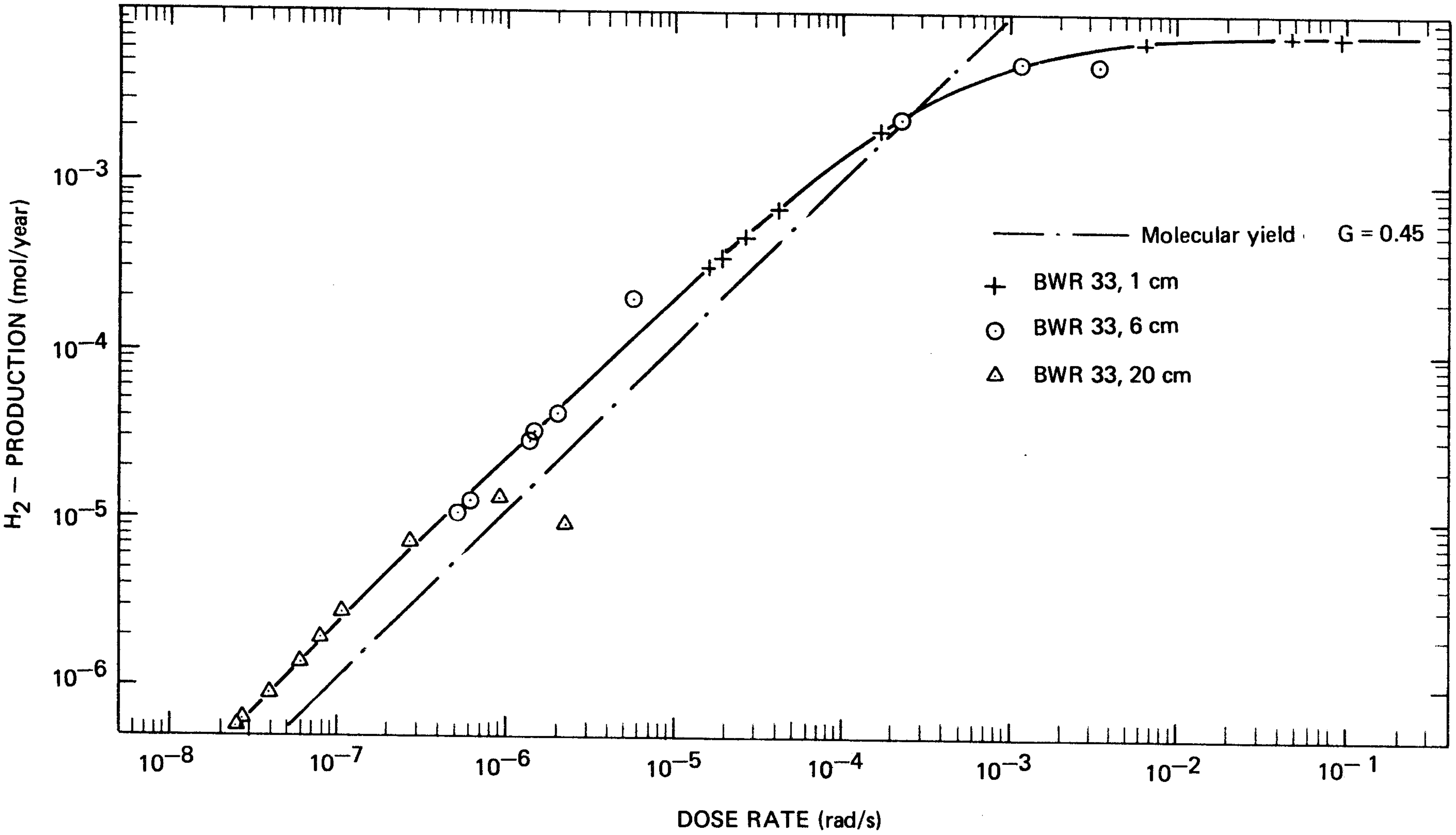

Figure 2. Hydrogen production as a function of dose rate. The radiation is absorbed in 720 l water. BWR 33, 1 cm means BWR fuel irradiated to 33 MWd/t, encapsulated in a copper canister with thickness of 1 cm.

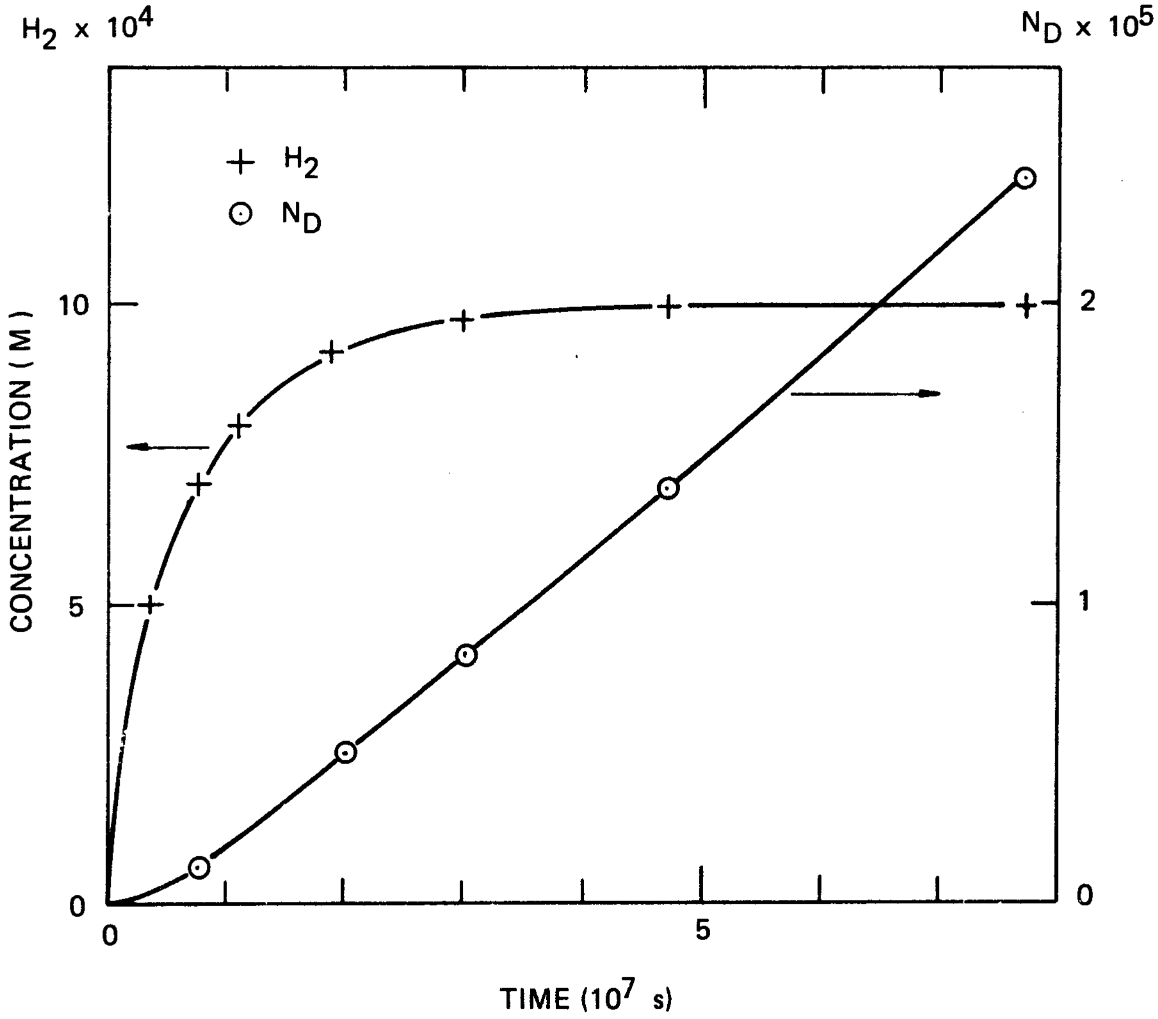

Figure 3. Yields of hydrogen and N_D (=hydrogen diffused away) as a function of time by γ-irradiation of water/bentonite outside a 1 cm copper canister at a storage time of 40 years.

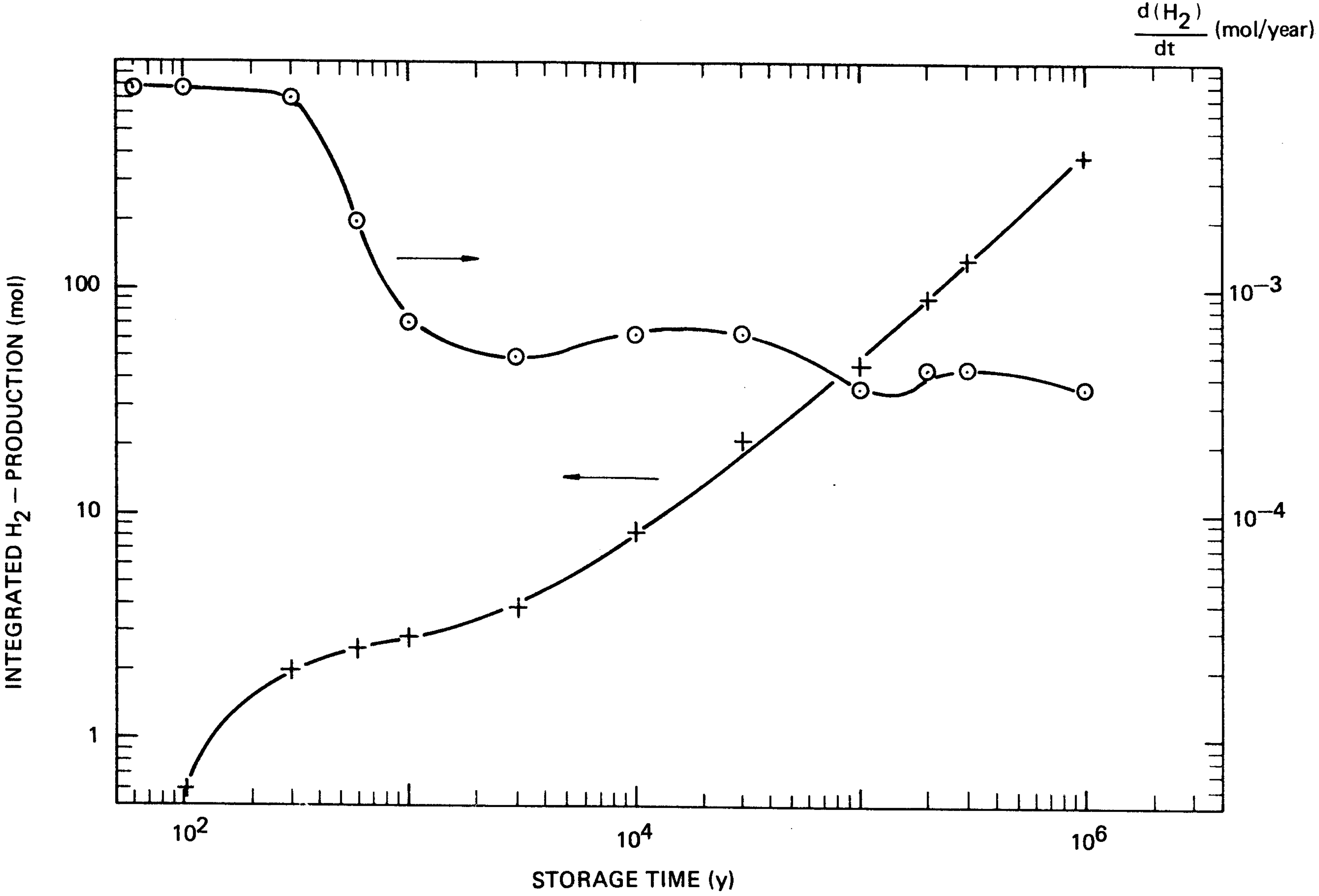

Figure 4. The integrated production and production rate of hydrogen as a function of time for BWR fuel, 33 MWd/t, 1 cm copper.

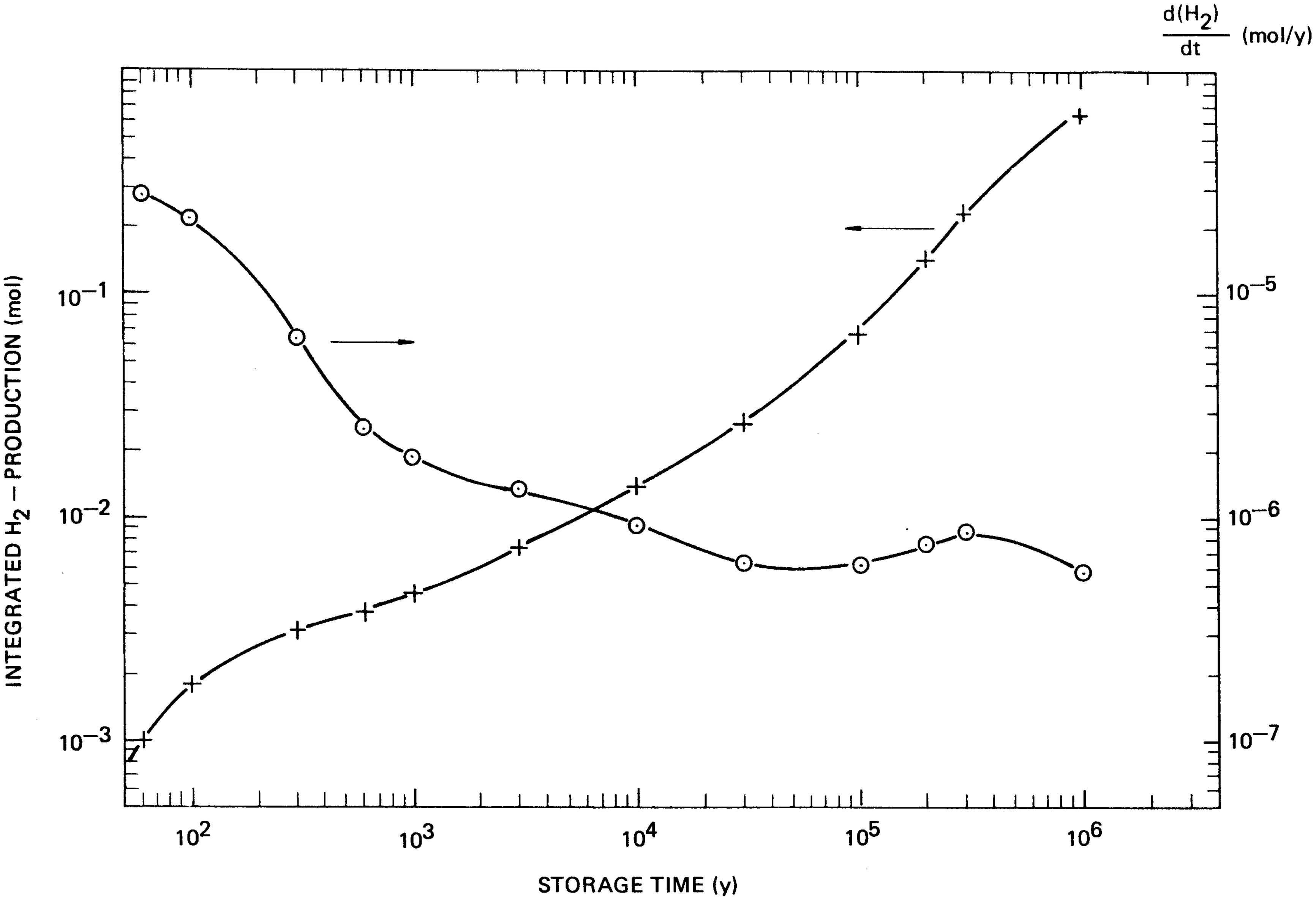

Figure 5. The integrated production and production rate of hydrogen as a function of time for BWR fuel, 33 MWd/t, 20 cm copper.

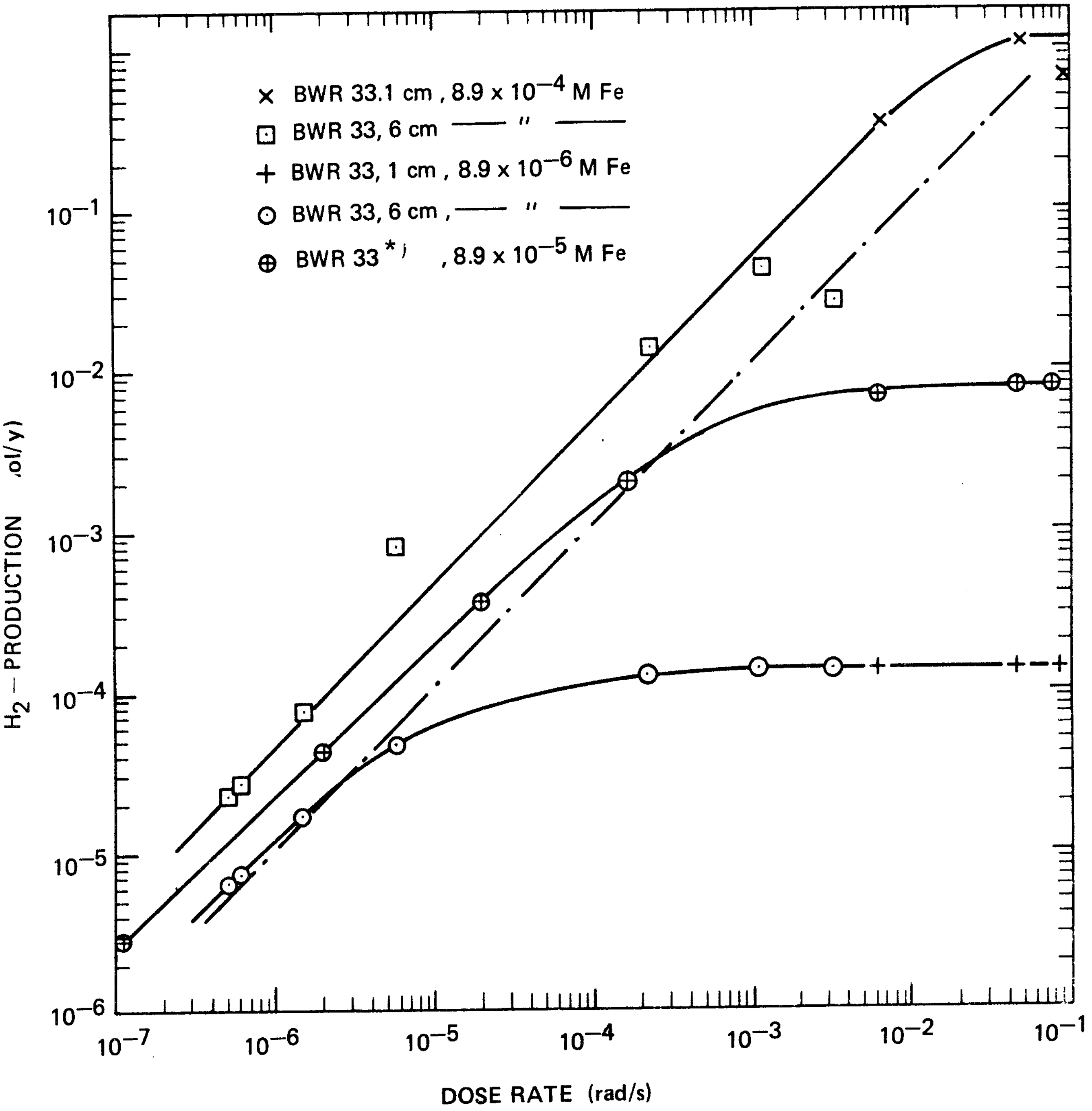

Figure 6. Hydrogen production as a function of dose rate for various iron concentrations in the water. The radiation is absorbed in 720 l water.
—— • —— $G(H_2) = 0.45$. *) Points corresponds to 1, 6 and 20 cm.

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. RADIOLYSIS OF GROUNDWATER FROM HLW STORED IN COPPER CANISTERS

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