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Radiolysis of ground water from spent fuel

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Studsvik Report

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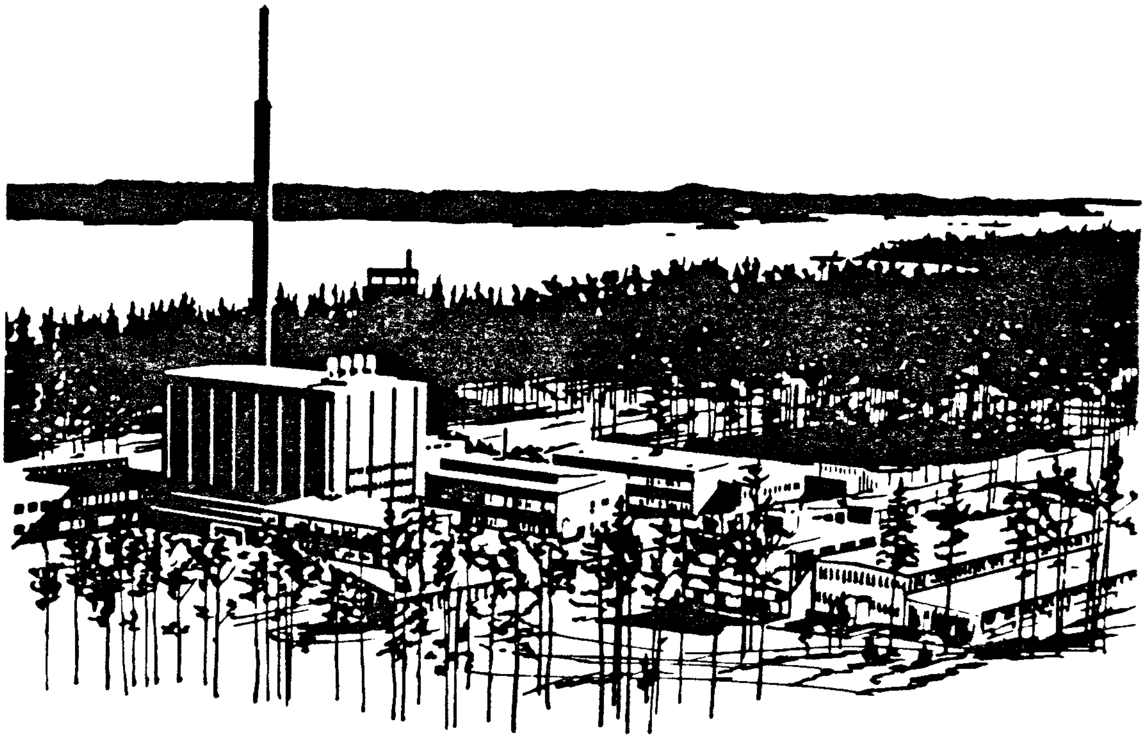

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Swedish Nuclear Fuel Safety Project

RADIOLYSIS OF GROUND WATER FROM SPENT FUEL

The effects of the radiolysis of water exposed to mixed alpha- and beta-radiation originating from spent fuel have been calculated. The water is 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 combined effects of alpha and beta-radiation, and the presence of iron in the water have been found to be important parameters. The beta-radiation will lower the yield of hydrogen, and so will the presence of low concentrations of iron ions. The most likely conditions for water exposed fuel give rise to a total production of 1 mol H_2 per m^2 fuel surface after 1 million years. A stoichiometric amount of oxygen is also formed.

The presence of an iron buffer, with a continuous supply of Fe^{2+} ions to the irradiated water phase increases the yield of hydrogen. After 1 million years the total hydrogen production is 70 mol per m^2 exposed fuel surface. A stoichiometric amount of Fe^{3+} is also formed.

If pure water is irradiated (i e iron is excluded) the yields of hydrogen and oxygen produced are high. The integrated production of hydrogen after 1 million years is 200 mol per m^2 exposed fuel surface. A stoichiometric amount of oxygen is also formed.

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Approved by

CONTENTS

1. INTRODUCTION

An excess of oxidizing radicals from the radiolysis of ground water ("oxrad") may create an oxidized region in the granitic host rock, which is normaly reducing due to its iron(II) content. The oxidizing radicals may increase the solubility of some radionuclides, and also increase their mobility within the oxidized zone (1). Molecular hydrogen is formed as a primary product in the radiolysis of water and - since it is relatively inactive - may be responsible for the excess of the oxidizing radicals.

We have previously made calculations of the radiolysis of ground water outside the canister, assuming varying wall thicknesses, and various iron contents in the water (2). The radiation outside the canister is mainly of the low LET type (beta and gamma). Therefore, recombination of hydrogen and hydrogen peroxide takes place to a considerable extent, and the total hydrogen yield (equal to the hydrogen which has diffused out of the system) is low (2).

In the present investigation calculations were carried out on the radiolysis of water which had penetrated the canister and fuel cladding, and thus had been exposed to the more densely ionizing alpha-radiation. Considerably higher yields of hydrogen may therefore be expected due to higher dose rates and less recombination of H_2 and H_2O_2.

2. EXPERIMENTAL CONDITIONS

2.1 Yields of primary radiolysis products

Whereas the yields for beta- and gamma-radiation are well known (3) this is not the case for alpha-radiation. Therefore comparisons have been made between measurements of hydrogen and oxygen carried out by Bibler (4) and calculations using the different sets of G-values:

1) Values given by Cohen (3), based mainly on data from Allen's monography (5).

2) Values calculated from data given by Bibler (4).

3) Burn's values (6) at a mean LET of 200 eV/nm.

4) An evaluated mean of the values 1-3.

5-6) Slightly modified values in an attempt to improve the agreement between the measured and calculated results.

The G-values used in the calculations are shown in Table 1, and the results of the calculations can be compared with the measured yields in Table 2. Set no 4 has been chosen for the subsequent calculations. The primary G-values from irradiation with beta-radiation and mixed alpha- and beta-radiation are also given in Table 1.

2.2 Irradiation dose

The dose rates used were based on calculations carried out by Klas Lundgren (7), who reported alpha, beta and gamma-dose rates in water containing pores of spent fuel, after storage times of 40 and 10^5 y, see Table 3. We have estimated dose rates at intermediate times and after 10^6y, based on decay curves of heavy nuclides (8), see

Table 3. The alpha-particle range was assumed to be 0.03 mm and we have, rather arbitrarily, chosen to present production in a volume of 4.32 l, determined by the range and the cylindrical surfaces of all fuel pellets in one canister, 144 m^2. This is also close to the gas void volume which is the maximum volume available for water intrusion.

2.3 Computer program

The program used, developed by Lang Rasmussen, Risö, Denmark is based on DIFSUB (9). 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 - if wanted - even after the irradiation. As an option the results can 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) irradiation dose and its duration.

a) and b) are given in Tables 4 and 5.

The predictive power of the program has been tested by comparing calculations using it with the results of experiments performed by T Eriksen and J Lind (10). In these experiments wet compacted bentonite clay was irradiated with gamma radiation, and the hydrogen production was measured. Various doses and bentonite/water ratios were tested. The correlation between measured and calculated results was very good (2). Simulations have also been performed successfully on experiments described in the literature (11).

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 can contain up to 3% iron, calculated as Fe_2O_3, but actually present in the reduced form (Fe^{2+}) (12). At present it is not known for certain to which degree, and at which rate this can be dissolved. We have, therefore, carried out calculations based on different assumptions. For most of the calculations we have assumed an initial Fe^{2+} concentration in the water of 5 ppm ($=8.9 \times 10^{-5}$M). Further we assumed that Fe^{3+} precipitates at concentrations above 1 ppm. In a few additional calculations we have assumed that the Fe^{2+} concentration is maintained at a constant of 8.9×10^{-5}M (i.e. we have assumed that the water at the fuel surface is in equilibrium with the water in the surrounding bentonite layer).

2.5 Diffusion of hydrogen and oxygen

The diffusion constant of hydrogen was calculated based on similar principles to those described previously (2). In most cases we have used a constant based on the diffusivity in bentonite ($2x10^{-11}$ m^2xs^{-1}). This is because we have assumed that the hydrogen must diffuse through the surrounding bentonite in order to escape from the system. In a few additional calculations we have used the diffusivity of pure water ($1.4x10^{-8}$ m^2xs^{-1}). The diffusivity of oxygen in bentonite is expected to be close to that of hydrogen in bentonite, therefore the same value was used (13).

3. RESULTS

3.1 Autoradiolysis of UO_2^{++} solutions

We have carried out some preliminary calculations on the radiolysis of UO_2^{++} solutions making the following assumptions:

- Dose rate: 56 rad x s^{-1} (only alpha-radiation)
- Initial concentration of UO_2^{++}: $10^{-3}M$
- Initial concentration of O_2:$2.4x10^{-4}M$ (aerated solutions at 0.1 MPa)
- Solubility of U(IV)(UO_2): $10^{-8}M$
- Reaction mechanism and rate constants: as shown in Tables 4 and 6.

Only in a few cases are the rate constants known. We have therefore used some of the rate constants as parameters, and the results can be seen in Table 7. The conclusion from these calculations is that with the current lack of knowledge concerning rate constants, any value for the equilibrium concentrations of UO_2^{++} can be obtained. Apparently the OH radicals do not react with UO_2 or UO_2^{+} because the H_2O_2 concentration is high enough to scavenge all the OH radicals.

3.2 Radiolysis of water from spent BWR and PWR fuel

Calculations have been carried out from 40 to 10^6 y on radiolysis from BWR fuel with a burnup of 33 Mwd/t, and PWR fuel with a burn up of 38 Mwd/t. In these calculations, we have assumed an initial Fe^{2+} buffert of 2.0 mol to be present in 4.3 l of H_2O (4.3 l H_2O corresponds to a surface layer of 144 m^2 fuel). We have used the diffusivities in bentonite in the calculations. As long as Fe^{2+} is added to the system the radiolysis products are hydrogen and Fe^{3+}, and the G-values are high. The Fe^{2+} buffer is consumed in a short time (less than 1 year). When the iron buffer has been consumed, $G(H_2)$ decreases by three orders of magnitude. The reason for this is that Fe^{2+} and Fe^{3+} are present and this redox couple acts as a recombiner, see equations 14, 32 and 35, in Tables 4 and 5. The results are presented as G-values, hydrogen production and integrated hydrogen production in Table 8 for BWR fuel, and in Table 9 for PWR fuel. The integrated production for both BWR and PWR fuel is low, less than 150 mol after 1 million years. This is the amount produced in 4.3 l of water which corresponds to a surface layer of 144 m^2: the integrated production in 1 million years is about 1 mol per m^2 surface area.

3.3 Effect of diffusivity

Using the diffusivities in bentonite the H_2-concentration in water irradiated with 40 y old BWR33 fuel increased to the saturation concentration, 3.9×10^{-2}M (at 5 MPa), within 49 d. After an additional 250 d irradiation the Fe^{2+} (2 mol) present initially had been oxidized and an equivalent amount of hydrogen (1.0 mol) had been formed, see Table 10. During these 250 d hydrogen bubbles are formed. After that the hydrogen disappears by diffusion at a rate of about 10^{-3} mol/y (between 40 and 100 y). $G(H_2)$ decreases from 0.26 during the period when Fe^{2+} is added continuously, to a value of only 1.8×10^{-4} when the Fe^{2+} buffer is consumed. The reason for the low value of $G(H_2)$ is probably that Fe^{2+} and Fe^{3+} act as recombiners, without being consumed:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \qquad 32$$
$$OH + H_2 \rightarrow H_2O + H \qquad 14$$
$$Fe^{3+} + E \rightarrow Fe^{2+} + OH^- \qquad 35$$

The hydrogen production decreases slowly with decreasing dose rate, see Table 10.

Using the diffusivities in water ($D(H_2) = 1.4 \times 10^{-8}$ $m^2 \times s^{-1}$, $D(O_2) = 5 \times 10^{-9}$ $m^2 \times s^{-1}$) the Fe^{2+} present initially (2.0 mol in 4.32 l) is consumed in 92 d, with the formation of 1.0 mol of hydrogen. The diffusion of hydrogen is fast enough to avoid the formation of hydrogen bubbles. After the consumption of Fe^{2+} hydrogen diffuses out of the system at the rate of 0.6 mol/y. At the same time oxygen diffuses out at the rate of 0.3 mol/y. The rates decrease considerably with decreasing dose rate, see Table 10. A more systematic variation of the diffusivities has also been carried out. The diffusion rate constants K28 and K28a, were varied from $5.77 \times 10^{-8} s^{-1}$ to $5.77 \times 10^{-5} s^{-1}$ in water containing 10^{-5}M Fe. In Table 11 it can be seen that the hydrogen production increases almost linarly with the diffusion rate constant, at least at small values of $G(H_2)$.

From these calculations it is obvious that the diffusivity is an important quantity in the system.

3.4 Effect of beta-radiation

In the previous calculations we have assumed a mixed alpha and beta-radiation field, see §2.2. In some preliminary calculations (13) we assumed a pure alpha-radiation field. The following calculation was made in order to study specifically the effect of a beta-radiation contribution.

The primary yields of radicals are considerably higher for beta-radiation than for alpha-radiation. A higher extent of recombination may therefore be expected in the presence of beta-radiation, and consequently lower productions of hydrogen and oxygen. This is indeed the case, as can be seen from Table 12. However, the yields for pure alpha-radiation are lower in the present calculation compared with the preliminary calculations (14). The reason for this is probably the presence of Fe^{2+}/Fe^{3+} in equilibrium concentrations. As noted previously this redox couple acts as a recombiner.

3.5 Continuous addition of Fe^{2+}

In the bulk of the calculations we have assumed a Fe^{2+} buffer of 2.0 mol in 4.3 l of water to be present initially (4.3 l water corresponds to a fuel surface of 144 m^2). This iron content is consumed in less than one year after the start of irradiation with 40 y old fuel, see Table 10. However, we have studied the consequences of the following assumption: during the long irradiation times it is possible that Fe^{2+} may be transported from the surrounding bentonite to the water layer at the surface of the fuel, so that this water keeps its initial Fe^{2+} concentration. The results can be seen in Table 13. The radiolysis products are Fe^{3+} (precipitated) and hydrogen (which has disappeared out of the system mainly by bubble formation).

The G-values are high, and the integrated hydrogen production after 1 million years is 10 000 mol. This amount has been produced in 4.3 l of H_2O, which corresponds to a fuel surface layer of 144 m^2. The integrated production per m^2 surface layer is 70 mol in 1 million years.

3.6 Effect of iron concentration

Calculations were carried out with total iron concentrations of 1, 10 and 50 μM. In these calculations there is no continuous addition of iron to the system.

Solutions with 10 and 50 μM iron yield nearly identical results with $G(H_2)=(1.3-1.5)\times10^{-4}$, see Table 14; but in the solution with a low iron content, 1 μM, the H_2O_2 is decomposed to a lesser extent (Equation 32), and less OH is produced.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \qquad \text{Eq 32}$$

Therefore the equilibrium concentration of hydrogen is higher as is the hydrogen production, see Table 14.

3.7 Irradiation of pure water with spent fuel

As a continuation of §3.6 we have made calculations for pure water with mixed alpha and beta-radiation corresponding to BWR33 fuel. The results are presented in Table 15. The hydrogen disappears mainly by bubble formation for the first 10^5 y. After this the hydrogen equilibrium concentration is below the solubility limit, which means that diffusion can remove the hydrogen produced. The solubilities of hydrogen and oxygen at 5MPa are 3.9×10^{-2}M and 6.45×10^{-2}M, respectively. As the gas bubbles are composed of 2/3 hydrogen and 1/3 oxygen the solubility limits of hydrogen and oxygen are 2.6×10^{-2} and 2.15×10^{-2} M, respectively. The yields of both hydrogen and oxygen are high with G-values of 0.9 and 0.45 for hydrogen and oxygen respectively. The equilibrium concentration of hydrogen peroxide is high, approximately 0.4 M. This is because the water is assumed to be very pure so that no catalytic decomposition of H_2O_2 takes place. The integrated production of hydrogen after 1 million years is 29000 mol in 4.3 l of water (144 m^2 surface). The production per m^2 is 200 mol hydrogen after 1 million years.

In the case of irradiation of pure water the effect of adding beta-radiation to the alpha-radiation can be assumed to be much less than in the case of irradiation of water containing iron ions, see Table 12. Apparently, the hydrogen yield for mixed alpha and beta-radiation is only about 20% lower than for pure alpha-radiation in the case of pure water.

4. CONCLUSIONS

The production of hydrogen is low under the conditions considered, which are most likely to prevail if water enters the canister and comes in contact with the fuel. The total production is 1 mol H_2 per m^2 exposed fuel surface after 1 million years (see Tables 8 and 9). An equivalent amount of oxygen is also formed. In 40 y old BWR33 fuel $G(H_2) = 1.8 \times 10^{-4}$. We have assumed the most likely conditions to be: water with a low content of iron (10^{-5}M); no further addition of iron; diffusion of hydrogen and oxygen at rates corresponding to their diffusivities in bentonite; a mixed alpha and beta-radiation field with a contribution of beta-radiation of 26%.

As other less likely conditions can not be excluded we have made calculations applicable to a number of conditions. In each of the following cases only one parameter at a time was changed from the basic conditions given above.

If an iron buffer is present, capable of a continuous addition of Fe^{2+} ions to the irradiated water phase, high yields of hydrogen are produced. After 1 million years the total hydrogen production is 70 mol per m^2 exposed fuel surface (see Table 13). A stoichiometric amount of Fe^{3+} is also formed. The hydrogen disappears mainly as bubbles.

If the diffusivities of pure water are used instead of the diffusivities in bentonite the yields are also high (see Table 10). The hydrogen production is of the order of 100 mol per m^2 after 10^6 y.

If the water is irradiated with alpha-radiation alone the initial hydrogen yield is 20 times higher than that for mixed alpha and beta-radiation ($G(H_2)=3.2x10^{-3}$ for 40 y old BWR33 fuel, see Table 12).

If pure water is irradiated (i e iron is excluded) high yields of hydrogen and oxygen are produced. The integrated production of hydrogen after 1 million years is 200 mol per m^2 exposed fuel surface (see Table 15). An equivalent amount of oxygen is also formed.

Acknowledgment

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TABLE 1. Primary G-values by radiolysis of water. The values are taken from various sources: 1) Allen-Cohen, 2) Bibler, 3) Burns, 4) "Best estimate", 5-6) modifications.

	α						β	α±β*
	1	2	3	4	5	6		
H_2	1.7	1.28	1.17	1.3	1.3	1.4	0.49	1.08
H	0.16	0.50	0.14	0.21	0.21	0.21	0.44	0.27
E^-	0.04	0.13	0.13	0.06	0.06	0.06	2.68	0.75
H_2O_2	1.3	0.98	0.92	0.985	1.00	1.10	0.74	0.92
HO_2	0.3	0.35	0.11	0.22	0.22	0.22	0.01	0.16
OH	0.1	0.18	0.44	0.24	0.21	0.21	2.59	0.86
H^+	0.04	0.13	0.13	0.06	0.06	0.06	2.77	0.77
$-H_2O$	3.34	2.97	2.63	2.71	2.71	2.91	6.86	3.79

*The contribution of beta-radiation is 26%

TABLE 2. Yields of hydrogen and oxygen after irradiation of acid water solutions of ^{244}Cm with alpha radiation using different sets of G-values. Comparison with measured yields.

Set of G-values*	Assumed gas volume, ml	$G(H_2)$	$G(O_2)$
1	1	1.68	0.093
	5	1.70	0.11
2	5	1.27	-0.024
3	5	1.15	0.13
	10	1.15	0.14
4	5	1.29	0.097
5	5	1.29	0.084
6	5	1.39	0.085
Measured yields		1.27±0.07	0.17±0.06

*See Table 1 for explanation

TABLE 3. Dose rates on the surface of fuel pellets after various storage times.

		Dose rate in rad/s after various storage times in y						
		40	100	300	1000	10^4	10^5	10^6
BWR33	α	28	23	15	7	1.5	7.5E-2	3E-2
	β	10	6.9	4.5	2.1	0.45	1.7-2	9E-3
PWR38	α	32	26	17	8	1.7	8.6E-2	3.4E-2
	β	12	8.3	5.4	2.5	0.54	1.4E-2	1.1E-2

TABLE 4. 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	5.77E-8
RE28a: O_2 = Dummy	5.77E-8

TABLE 5. Additional reactions 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 6. Additional reactions in the presence of UO_2^{++}

28. UO_2 -> Dummy; E7
29. Dummy -> UO_2; 1
30. UO_2^{++} + e^- -> UO_2^+ + H_2O: 2E10
31. UO_2^+ + UO_2^+ -> UO_2^{++} + UO_2; E7 eller E10
32. UO_2^+ + OH -> UO_2^{++} + OH^-; 2E9
33. UO_2 + OH -> UO_2^+ + OH^-; 2E9
34. UO_2^+ + e^- -> UO_2 + H_2O; 5E9
35. UO_2^+ + H_2O_2 -> UO_2^{++} + OH + OH^-; 5E2
36. UO_2 + H_2O_2 -> UO_2^+ + OH + OH^-; 5E2
37. UO_2^+ + O_2^- -> UO_2^{++} + O_2^{--}; 4E8
38. UO_2 + O_2^- -> UO_2^+ + O_2^{--}; 4E8
39. UO_2^{++} + O_2^- -> UO_2^+ + O_2; 4E8
40. O_2^{--} + H_2O -> HO_2^- + OH^-; E4
41. UO_2^+ HO_2 -> UO_2^{++} + HO_2^-; 4E8
42. UO_2 + HO_2 -> UO_2^+ + HO_2^-; 4E8
43. UO_2^{++} - HO_2 -> UO_2^+ + O_2 + H^+; 4E8

TABLE 7. Autoradiolysis of aerated UO_2^{++} solutions. $C_o(UO_2^{++})=10^{-3}M$, dose rate = 56 $radxs^{-1}$ (alpha-radiation).

Conc. after 24 h irradiation, $10^{-3}M$						
	H_2	H_2O_2	O_2	UO_2^{++}	Dummy*	Comments
1	4.85	3.97	1.18	$2.6x10^{-5}$	1.0	K31=E10
2	3.51	2.09	1.45	$1.7x10^{-4}$	1.0	K31=E7
3	3.51	2.09	1.44	$1.6x10^{-2}$	1.0	K31=E7; K39=K43=4E6
4	2.66	1.20	1.46	$2\text{-}0x10^{-2}$	1.0	Like 3 but K35=K36=E3
5	3.42	2.1	1.19	0.42	0.6	" 4 " K37,K38,K41,K42 = E10

* Dummy = UO_2, which has precipitated

TABLE 8. Hydrogen production in water irradiated with mixed alpha and beta-radiation from BWR fuel with a burn-up of 33 MWd/t.

Storage time y	$C(H_2)$ at eq. µM	$G(H_2)$	Hydrogen* production mol/y	Integrated** production mol
41	120	1.8xE-4	9.8E-4	0
100	105	1.9xE-4	8.3E-4	5.4E-2
300	84	2.4xE-4	6.7E-4	2.0E-1
1000	58	3.5xE-4	4.6E-4	6.0E-1
10^4	31	8.9xE-4	2.5E-4	3.84
10^5	22	1.3xE-2	1.8E-4	23
10^6	11	1.6xE-2	0.9E-4	143

* Production in 4.3 l H_2O corresponding to a fuel surface of 144 m^2.

** In addition 1 mol of hydrogen is produced initially during the period of consumption of the iron buffert.

TABLE 9. Hydrogen production in water irradiated with mixed alpha and beta-radiation from PWR fuel with a burn-up of 38 MWd/t.

Storage time y	$C(H_2)$ at eq. µM	$G(H_2)$	Hydrogen* production mol/y	Integrated** production mol
41	137	1.7E-4	1.089E-3	0
100	121	1.8E-4	9.68E-4	6.2E-2
300	94	2.2E-4	7.47E-4	2.3E-1
1000	63	3.3E-4	5.05E-4	6.7E-1
10^4	34	7.9E-4	2.69E-4	4.2
10^5	22	1.3E-2	1.79E-4	24
10^6	12	1.4E-2	9.33E-5	147

* Production in 4.3 l H_2O corresponding to a fuel surface of 144 m^2.

**In addition 1 mol of hydrogen is produced initially during the period of consumption of the iron buffert.

TABLE 10. Irradiation of water using diffusivities in pure water or in bentonite.

	Storage time y	Diffusivities valid for	Irradiated until	$G(H_2)$	Total H_2 production in 4.32 l mol/y
1	40	H_2O	92 d	0.72	1.0 (in 92 d)
2	40	H_2O	100 d	0.11	0.6
3	E5	H_2O	3E5y	0.81	0.010
4	40	Bentonite	49 d	0.28	0.19 (in 49 d)
5	40	"	270 d	0.26	1.0 (in 270 d)
6	40	"	100 y	1.8E-4	9.8E-4
7	E5	"	3E5 y	1.5E-2	1.9E-4

	Comments	
1		Iron added continuously
2	Equilibrium conc	Iron has been consumed
3		" " " "
4	Saturation of H_2 obtained ($C(H_2)=3.9\times10^{-2}M$)	Iron added continuiously
5	H_2 disappears by bubble formation	Iron has been consumed
6	Equlibrium after 8 y	

TABLE 11. Effect of diffusion rate constants on the hydrogen yield by mixed alpha- and beta-irradiation of H_2O containing 10^{-5}M Fe.

Storage time y	K_D* s^{-1}	Equilibrium conc. Fe^{2+} µM	Fe^{3+}	H_2	H_2O_2	$G(H_2)$	H_2 production mol/y
40	5.77E-8	3.2	6.8	123	125	1.8E-4	9.8E--4
40	5.77E-7	3.2	6.8	122	125	1.8E-3	9.8E-3
40	5.77E--6	3.2	6.8	118	123	1.8E-2	9.8E-2
40	5.77E-5	3.2	6.8	90	107	0.13	0.72
E5	5.77E-8	1.2	8.8	22	1.4	1.4E-2	1.8E-4
E5	5.77E-7	1.1	8.9	17	1.5	0.11	1.4E-3
E5	5.77E-6	0.7	9.3	6.7	1.9	0.42	5.4E-3
E5	5.77E-5	0.4	9.6	1.4	2.4	0.87	1.1E-2

*The same diffusion rate constant is used for H_2 and O_2.

TABLE 12. Effect of beta-radiation. Total dose rate 44 rad/s. Iron concentration 10^{-5}M.

Radiation source	β-contribution, %	Equilibrium conc. µM Fe^{2+}	Fe^{3+}	H_2	H_2O_2	$G(H_2)$	$P(H_2)$* mol/y
α	0	1.9	8.1	2600	490	3.2×10^{-3}	2.0×10^{-2}
α+β	26	3.3	6.7	137	143	1.7×10^{-4}	1.1×10^{-3}

*Hydrogen production in 4.3 l H_2O, corresponding to a fuel surface of 144 m^2.

TABLE 13. Radiolysis of water with mixed alpha and beta-radiation. Continuous addition of Fe^{2+}. BWR fuel.

Storage	Equilibrium concentration, µM				$G(H_2)$	$P(H_2)$*	$IP(H_2)$**
time, y	Fe^{2+}	Fe^{3+}	H_2	H_2O_2		mol/y	mol
40	85	10	3900	4.8	0.20	1.04	0
100	85	10	3900	4.0	0.23	0.91	58
300	86	10	3900	3.0	0.26	0.70	219
1000	87	10	3900	1.7	0.30	0.39	601
10^4	87	10	3900	0.4	0.35	0.096	2800
10^5	88	10	3900	0.02	0.37	0.0048	6900
10^6	88	10	3900	0.01	0.37	0.0020	9800

*Hydrogen production in 4.3 l H_2O corresponding to a fuel surface of 144 m^2.

**Integrated production.

TABLE 14. Effect of iron concentration (no continuous supply of iron) PWR38, 40 y (44 rad x s^{-1})

Total iron	Equilibrium conc, µM			H_2O_2	$G(H_2)$	$P(H_2)$*
conc. µM	Fe^{2+}	Fe^{3+}	H_2			mol/y
1	0.39	0.61	761	1070	7.3E-4	6.0E-3
10	3.3	6.7	137	143	1.3E-4	1.1E-3
50	10	40	152	65	1.5E-4	1.2E-3

*Hydrogen production in 4.3 l H_2O, corresponding to a fuel surface of 144 m^2.

TABLE 15. Irradiation of pure water with mixed alpha and beta-radiation. BWR fuel.

Storage time, y	Equilibrium conc,mM H_2	O_2	$G(H_2)$	$P(H_2)$* mol/y	$IP(H_2)$** mol
40	26	21.5	0.93	4.9	0
100	26	21.5	0.93	3.6	260
300	26	21.5	0.93	2.5	860
1000	26	21.5	0.93	1.17	2100
10^4	26	21.5	0.93	0.25	8600
10^5	1.7	1.2	1.01	0.0130	20600
10^6	0.74	0.64	1.08	0.0060	29000

*Hydrogen production in 4.3 l H_2O corresponding to a fuel surface of 144 m^2.

**Integrated production.

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