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Assessment of homogeneous processes and parameters to be used in models for radiation induced dissolution of spent nuclear fuel

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This report concerns a study which was conducted for Svensk Kärnbränslehantering AB (SKB). The conclusions and viewpoints presented in the report are those of the authors. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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Abstract

In this work, radiation chemical yields for alpha radiolysis and reaction sets including rate constants for radiation induced reactions in aqueous solution have been critically assessed. State of the art data sets have been identified with the recommendation to be used when modelling the homogeneous radiation chemistry as part of a more complex model describing radiation induced dissolution of spent nuclear fuel under deep repository conditions.

Sammanfattning

I detta arbete har strålningskemiska utbyten för alfaradiolys samt set av reaktioner med tillhörande hastighetskonstanter kritiskt granskats. Dataset som utgör state of the art har identifierats och rekommenderas för användning vid simulering av homogen strålningskemi som en del av en mer komplex modell som beskriver strålningsinducerad upplösning av utbränt kärnbränsle under djupförvarsbetingelser.

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1 Introduction

Radiation induced dissolution of spent nuclear fuel is a process of key-relevance in the safety assessment of geological repositories for spent nuclear fuel as this process could potentially result in the release and spreading of radiotoxic elements into the biosphere. Ionizing radiation emitted from the used nuclear fuel will induce radiolysis of groundwater in contact with the fuel in the event of multiple barrier failure. Radiolysis of water produces oxidants (OH^\cdot , HO_2^\cdot and H_2O_2) and reductants (e_{aq}^- , H^\cdot and H_2) with sufficient reactivity to induce chemical reactions on the fuel surface (Shoesmith 2000). The oxidants drive the oxidative dissolution while the reductants can inhibit the process under certain conditions. To enable prediction of the long-term behavior of spent nuclear fuel under repository conditions, numerical simulations taking water radiolysis and the subsequent reactions in water as well as the surface reactions into account are needed. The quality and reliability of such simulations largely depend on the use of verified reaction mechanisms and rate parameters. To describe the radiation chemistry of water, the radiation chemical yields as well as a set of reactions and their corresponding rate constants must be used. At times relevant in the safety assessment, i.e., more than 1 000 years after closure, the dominating type of ionizing radiation at the fuel surface is alpha-radiation (Shoesmith 2000).

Numerous experimental and modeling studies on radiation-induced dissolution of spent nuclear fuel have been carried out over the past four decades. From these studies we can learn how to simplify the reaction system to some extent. One example is the finding that radiation induced dissolution of spent nuclear fuel is dominated by H_2O_2 and that the other radiolytic oxidants have a very marginal direct impact on the fuel oxidation (Ekeröth et al. 2006). Another example is the fact that the system soon reaches steady-state which can allow for considerably simpler numerical models (Jonsson et al. 2007). Even though simplifications can be very useful, there is also a risk that some reactions or species could be overlooked. To avoid this and to enable testing and verification of new reaction mechanisms and their corresponding rate constants, it is essential to have access to numerical models where as few simplifications as possible have been made. This requires complete reaction sets and correctly described dose rate profiles.

2 Assessment

2.1 Model requirements

A complete numerical model describing radiation induced dissolution of spent nuclear fuel should consist of the following parts: (i) geometrical dose distribution based on radionuclide inventory, (ii) kinetic model describing reactions in homogeneous solution, (iii) kinetic model describing surface reactions, and (iv) model describing diffusion between volume elements since the surface reactions as well as the dose rate profile give rise to concentration gradients.

This report is devoted to the kinetic model describing reactions in homogeneous solution. A kinetic model describing reactions in homogeneous solution includes radiation chemical yields (G-values) as well as reactions and rate constants for radiation induced reactions in water. In addition, reactions of solutions containing $\text{HCO}_3^-/\text{CO}_3^{2-}$ are included. A future report will be focused on the kinetic model describing surface reactions (Assessment of heterogeneous processes and parameters to be used in models for radiation induced dissolution of spent nuclear fuel).

Upon screening the literature, it is obvious that radiation chemical yields as well as reaction sets vary. The objective of this report is to identify state of the art radiation chemical yields and reaction sets to be used in the development of a numerical model for radiation induced dissolution of spent nuclear fuel.

2.2 Radiation chemical yields (G-values)

The radiation chemical yield is defined as the amount of reactant consumed or product formed per energy unit of absorbed radiation. Traditionally the unit molecules per 100 eV is used but the SI-unit is mol J^{-1} . Radiation chemical yields in a given liquid at a given temperature depend on the type and energy of radiation as well as on time. The reason for the time-dependence is that the original interaction between ionizing radiation and matter in general is highly localized resulting in a heterogeneous system (Mozumder 1999). As species formed in localized interactions diffuse away and also react with other species, the yields change. When studying the radiation chemistry of dilute systems, i.e., where the concentration of solutes reactive towards radiolysis products is low, the homogeneous G-values must be used. In concentrated solution, where the solutes may react with the radiolysis products before the solution can be regarded as homogeneous, the homogeneous G-values are not valid. Granitic groundwater can in general be regarded as dilute and therefore we should use the homogeneous G-values. It should be noted that for the water layers adjacent to the fuel surface, homogeneous G-values may not be representative.

As alpha radiation will dominate the radiation field close to the fuel surface, this report is focused on G-values for alpha-radiolysis of water at room temperature.

In Table 2-1, radiation chemical yields from five different sources are presented. Some of them are presented in the unit molecules per 100 eV in the original work. To enable direct comparison, all G-values have been converted to the unit $\mu\text{mol J}^{-1}$.

Table 2-1. G-values for He^{2+} -radiolysis of water in $\mu\text{mol J}^{-1}$.

	Pastina and LaVerne (2001)	Poinssot et al. (2004)	Buck et al. (2012)	Choppin et al. (2002)	Christensen and Bjergbakke (1985)
e^-_{aq}	0.016	0.0062	0.016	0.0044	0.0062
$\text{H}\cdot$	0.010	0.022	0.010	0.028	0.022
H_2	0.12	0.13	0.12	0.12	0.13
$\text{OH}\cdot$	0.036	0.026	0.036	0.056	0.025
H_2O_2	0.10	0.10	0.10	0.11	0.10
$\text{HO}_2\cdot$	0.010	0.023	0.010	0.007	0.023
H^+	0.019	0.0062	0.019	--	0.0062
OH^-	0.0031	--	--	--	--

As can be seen, the G-values vary considerably between the different sources. However, it should be noted that the G-values for the dominating products (H_2O_2 and H_2) vary by less than 10 % between all the data sets.

It is also obvious that some of the sources present identical sets. Poinssot et al. (2004) uses the same data as Christensen and Bjergbakke (1985) while Buck et al. (2012) uses data from Pastina and LaVerne (2001). The data from Choppin et al. (2002) is valid for 12 MeV He^{2+} which is considerably higher than the 5 MeV relevant for alpha-radiation emitted from spent nuclear fuel. The particle energy for the set in Christensen and Bjergbakke (1985) is not clearly stated while the set from Pastina and LaVerne (2001) is valid for 5 MeV. Furthermore, Pastina and LaVerne (2001) made use of previously published G-values and material balance to make a first estimation of escape yields (the homogeneous G-values). The escape yields were then varied until predicted results matched experimental results. The set presented by Pastina and LaVerne (2001) can be seen as the state of the art in view of the experimental data available at the time of the publication. No rigorous revision of the G-values for alpha-radiolysis has been published after the work by Pastina and LaVerne (2001). In conclusion, the G-values by Pastina and LaVerne (2001) should be used when modelling alpha-radiolysis.

2.3 Reactions and rate constants

The number of possible reactions that can occur in pure water upon radiolysis is quite high. One reason for this is that reactions can occur with species in different states of protonation. It is often possible to exclude some reactions on the basis of pH but a general set should include reactions to account for a wide pH-range. Four sets of reactions and rate constants have been identified as particularly interesting when describing the radiation chemistry of pure water. These sets are presented in Table 2-2.

Table 2-2. Reactions and rate constants (in $dm^3 mol^{-1} s^{-1}$ or s^{-1}) used when simulating radiation chemistry in aqueous systems.

No	Reaction	Pastina and LaVerne (2001)	Poinssot et al. (2004)	Elliot and Bartels (2009)	Meesungnoen and Jay-Gerin (2010)
1	$H^+ + OH^- \rightarrow H_2O$	1.4×10^{11}	1.43×10^{11}		1.12×10^{11}
2	$H_2O \rightarrow H^+ + OH^-$	2.5×10^{-5}	2.6×10^{-5}		
3	$e_{aq}^- + H_2O \rightarrow H \cdot + OH^-$	19	19		15.8
4*	$2e_{aq}^- (+2H_2O) \rightarrow H_2 + 2OH^-$	5.5×10^9	5.5×10^9	6.2×10^9	5.0×10^9
5*	$e_{aq}^- + H \cdot (+H_2O) \rightarrow H_2 + OH^-$	2.5×10^{10}	2.5×10^{10}	2.5×10^{10}	2.5×10^{10}
6	$e_{aq}^- + OH \cdot \rightarrow OH^-$	3.0×10^{10}	3.0×10^{10}	3.34×10^{10}	2.95×10^{10}
7*	$e_{aq}^- + O^- (+H_2O) \rightarrow 2OH^-$	2.2×10^{10}			2.31×10^{10}
8	$e_{aq}^- + H^+ \rightarrow H \cdot$	2.3×10^{10}	2.3×10^{10}		2.11×10^{10}
9	$e_{aq}^- + H_2O_2 \rightarrow OH^- + OH \cdot$	1.1×10^{10}	1.1×10^{10}	1.22×10^{10}	1.1×10^{10}
10	$e_{aq}^- + HO_2^- \rightarrow O^- + OH^-$	3.5×10^9	3.5×10^9		3.51×10^9
11	$e_{aq}^- + HO_2 \cdot \rightarrow HO_2^-$	2.0×10^{10}	2.0×10^{10}	1.19×10^{10}	1.28×10^{10}
12	$e_{aq}^- + O_2 \rightarrow O_2^-$	1.9×10^{10}	1.9×10^{10}	2.11×10^{10}	1.74×10^{10}
13*	$e_{aq}^- + O_2^- (+H_2O) \rightarrow HO_2^- + OH^-$	1.3×10^{10}	1.3×10^{10}	1.19×10^{10}	1.3×10^{10}
14	$H \cdot + H_2O \rightarrow H_2 + OH \cdot$	11			
15	$H \cdot + H \cdot \rightarrow H_2$	7.8×10^9	7.8×10^9	4.62×10^9	5.03×10^9
16	$H \cdot + OH \cdot \rightarrow H_2O$	7.0×10^9	7.0×10^9	1.03×10^{10}	1.55×10^{10}
17	$H \cdot + OH^- \rightarrow e_{aq}^-$	2.2×10^7	2.2×10^7		2.51×10^7
18	$H \cdot + H_2O_2 \rightarrow OH \cdot + H_2O$	9.0×10^7	9.0×10^7	3.16×10^7	3.5×10^7
19	$H \cdot + O_2 \rightarrow HO_2 \cdot$	2.1×10^{10}	2.1×10^{10}	1.2×10^{10}	2.1×10^{10}
20	$H \cdot + O_2^- \rightarrow HO_2^-$	1.8×10^{10}	2.0×10^{10}	1.03×10^{10}	1.0×10^{10}
21	$H \cdot + HO_2 \cdot \rightarrow H_2O_2$	1.8×10^{10}	1.0×10^{10}		1.0×10^{10}
22	$H \cdot + HO_2^- \rightarrow 2OH^-$			1.03×10^{10}	
23	$OH \cdot + OH \cdot \rightarrow H_2O_2$	3.6×10^9	5.5×10^9	4.54×10^9	5.5×10^9
24	$H \cdot + HO_2^- \rightarrow OH^- + OH^-$	9.0×10^7			1.46×10^9
25	$OH \cdot + O^- \rightarrow HO_2^-$	2.5×10^{10}			1.0×10^9
26	$OH \cdot + H_2 \rightarrow H \cdot + H_2O$	4.3×10^7	3.4×10^7		3.28×10^7
27	$OH \cdot + OH^- \rightarrow O^- + H_2O$	1.3×10^{10}	1.3×10^{10}	1.18×10^{10}	6.3×10^9

No	Reaction	Pastina and LaVerne (2001)	Poinssot et al. (2004)	Elliot and Bartels (2009)	Meesungnoen and Jay-Gerin (2010)
28	$OH \cdot + H_2O_2 \rightarrow H_2O + HO_2 \cdot$	2.7×10^7	2.7×10^7	2.65×10^7	2.87×10^7
29	$OH \cdot + HO_2^- \rightarrow OH^- + HO_2 \cdot$	7.5×10^9	7.5×10^9		8.32×10^9
30	$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	5.74×10^4			3.83×10^4
31	$OH \cdot + HO_2 \cdot \rightarrow H_2O + O_2$	6.0×10^9	6.6×10^9	8.44×10^9	7.9×10^9
32	$OH \cdot + O_2^- \rightarrow OH^- + O_2$	8.2×10^9	1.0×10^{10}	1.02×10^{10}	1.07×10^{10}
33	$O^- + H_2O \rightarrow OH^- + OH \cdot$	1.86×10^6	1.8×10^6	9.97×10^5	1.02×10^6
34*	$O^- + O^- (+H_2O) \rightarrow HO_2^- + OH^-$	1.0×10^9			1.0×10^8
35	$O^- + H_2 \rightarrow H \cdot + OH^-$	8.0×10^7			1.21×10^8
36	$O^- + H_2O_2 \rightarrow O_2^- + H_2O$	5.0×10^8			5.55×10^8
37	$O^- + HO_2^- \rightarrow O_2^- + OH^-$	4.0×10^8			3.5×10^8
38	$O^- + O_2 \rightarrow O_3^-$	3.6×10^9			3.7×10^9
39*	$O^- + O_2^- (+H_2O) \rightarrow 2OH^- + O_2$	6.0×10^8			6.0×10^8
40	$H_2O_2 \rightarrow H^+ + HO_2^-$	0.112	0.036		
41	$H^+ + HO_2^- \rightarrow H_2O_2$	5.0×10^{10}	2.0×10^{10}		5.0×10^{10}
42	$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1.3×10^{10}			4.75×10^8
43	$H \cdot \rightarrow e_{aq}^- + H^+$	3.91			
44	$O^- + H^+ \rightarrow OH \cdot$	1.0×10^{11}			4.78×10^{10}
45	$HO_2^- \rightarrow O_2^- + H^+$	1.35×10^6	8.0×10^5		
46	$O_2^- + H^+ \rightarrow HO_2$	5.0×10^{10}	5.0×10^{10}		4.78×10^{10}
47	$HO_2 + OH^- \rightarrow O_2^- + H_2O$	5.0×10^{10}			6.3×10^9
48	$O_2^- + H_2O \rightarrow HO_2 + OH^-$	1.0×10^3			0.075
49	$HO_2 + H_2O \rightarrow O_2^- + H^+$				1.29×10^4
50*	$e_{aq}^- + O_3^- (+H_2O) \rightarrow O_2 + 2OH^-$	1.6×10^{10}			
51	$e_{aq}^- + O_3 \rightarrow O_3^-$	3.6×10^{10}			3.6×10^{10}
52	$H + O_3 \rightarrow O_2 + OH$				3.7×10^{10}
53	$H \cdot + H_2O \rightarrow H_2 + OH \cdot$	11			
54	$H \cdot + O^- \rightarrow OH^-$	1.0×10^{10}			2.0×10^{10}
55	$H \cdot + HO_2^- \rightarrow OH \cdot + OH^-$	9.0×10^7			
56	$H \cdot + O_3^- \rightarrow OH^- + O_2$	1.0×10^{10}			1.0×10^{10}
57	$H \cdot + O_3 \rightarrow HO_3$	3.8×10^{10}			
58	$OH \cdot + O_3^- \rightarrow O_3 + OH^-$	2.6×10^9			
59	$OH \cdot + O_3^- \rightarrow 2O_2^- + H^+$	6.0×10^9			8.5×10^9
60	$OH \cdot + O_3 \rightarrow HO_2 + O_2$	1.1×10^8			1.11×10^8
61	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	8.0×10^7	9.6×10^7	9.47×10^7	9.7×10^7
62	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	7.0×10^5	8.4×10^5	7.31×10^5	8.3×10^5
63	$HO_2 + O^- \rightarrow O_2 + OH^-$	6.0×10^9			
64	$HO_2 + H_2O_2 \rightarrow OH \cdot + O_2 + H_2O$	0.50			
65	$HO_2 + HO_2^- \rightarrow OH \cdot + O_2 + OH^-$	0.50			
66	$HO_2 + O_3^- \rightarrow 2O_2 + OH^-$	6.0×10^9			
67	$HO_2 + O_3 \rightarrow HO_3 + O_2$	5.0×10^8			
68*	$2O_2^- (+2H_2O) \rightarrow H_2O_2 + O_2 + OH^-$	100	1.8×10^9		
69	$O_2^- + H_2O_2 \rightarrow OH \cdot + O_2 + OH^-$	0.13			
70	$O_2^- + HO_2^- \rightarrow O \cdot^- + O_2 + OH^-$	0.13			
71*	$O_2^- + O_3 (+H_2O) \rightarrow 2O_2 + 2OH^-$	1.0×10^4			
72	$O_2^- + O_3 \rightarrow O_3^- + O_2$	1.5×10^9			1.5×10^9
73	$O^- + O_3^- \rightarrow 2O_2^-$	7.0×10^8			7.0×10^8
74	$O^- + O_3 \rightarrow O_2^- + O_2$	5.0×10^9			
75	$O_3^- \rightarrow O_2 + O^-$	3.3×10^3			
76	$O_3^- + H^+ \rightarrow O_2 + OH \cdot$	9.0×10^{10}			9.0×10^{10}
77	$HO_3 \rightarrow O_2 + OH \cdot$	1.1×10^5			
78	$O_3^- + H_2O \rightarrow O_2 + O^-$				48
79	$OH^- \rightarrow H^+ + O^-$	0.13			

* Water is not included in the rate expression for which the rate constant is valid. To convert the rate constant to include also water, the tabulated value should be divided by $[H_2O]$ or $[H_2O]^2$ depending on if there is one or two water molecules among the reactants.

In total, 79 reactions are identified. The most obvious difference between the sets is the number of reactions. The first set (Pastina and LaVerne 2001) includes 75, the second set (Poinssot et al. 2004) includes 34, the third set (Elliot and Bartels 2009) includes 21 and the fourth set (Meesungnoen and Jay-Gerin 2010) includes 55 reactions. The two sets with fewer reactions generally miss ozone reactions and reactions involving the deprotonated hydroxyl radical, $O^{\cdot-}$. The latter is important for very alkaline systems.

As can be seen in the table, the rate constants do not vary much between the sets for the reactions covered by several sets. However, there is one important exception and that is reaction 68 (the disproportionation of superoxide) where the first set (Pastina and LaVerne 2001) uses $50 \text{ M}^{-1} \text{ s}^{-1}$ while the second set (Poinssot et al. 2004) uses $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This will most probably have a strong influence on the steady-state concentration of superoxide and possibly also on H_2O_2 in the system and can therefore be considered as a crucial parameter.

In many of the reactions describing acid-base equilibria it is important to reproduce the equilibrium constant. It is therefore important to check if a data set is consistent in terms of acid-base equilibria before taking it into use. The most complete set of reactions (the first set) was checked for consistency and the conclusion is that it is consistent. Another reason for selecting set 1 is the fact that this set was used in the G-value optimization procedure by Pastina and LaVerne (2001) and the combination of these two sets of data can be seen as more consistent than other combinations.

A generally available source for rate constants of reactions of relevance in aqueous radiation chemistry is the NIST database: NDRL/NIST Solution Kinetics Database on the Web, NIST Standard Reference Database 40 (<https://kinetics.nist.gov/solution/>). A cross comparison between set 1 (Pastina and LaVerne 2001) and the database was conducted. The results can be found in Table 2-3. The references in the table are stated using the same format as in the database.

Table 2-3. Comparison between set 1 (Pastina and LaVerne 2001) and a kinetic database (<https://kinetics.nist.gov/solution/>).

No	Reaction	Pastina and LaVerne (2001)	Database	Ref
1	$H^+ + OH^- \rightarrow H_2O$	1.4×10^{11}		
2	$H_2O \rightarrow H^+ + OH^-$	2.6×10^{-5}		
3	$e_{aq}^- + H_2O \rightarrow H \cdot + OH^-$	19	1.0×10^3	1992SCH8937-8941
4*	$2e_{aq}^- (+2H_2O) \rightarrow H_2 + 2OH^-$	5.5×10^9	5.5×10^9	1988BUX/GRE513-886
5*	$e_{aq}^- + H \cdot (+H_2O) \rightarrow H_2 + OH^-$	2.5×10^{10}	2.4×10^{10}	1994CHR/SEH527-531
6	$e_{aq}^- + OH \cdot \rightarrow OH^-$	3.0×10^{10}	2.8×10^{10}	1994ELL/OUE837-841
7*	$e_{aq}^- + O^{\cdot-} (+H_2O) \rightarrow 2OH^-$	2.2×10^{10}	2.2×10^{10}	1965MAT/RAB1324-1335
8	$e_{aq}^- + H^+ \rightarrow H \cdot$	2.3×10^{10}	2.4×10^{10}	1994SHI/SUN5164-5173
9	$e_{aq}^- + H_2O_2 \rightarrow OH^- + OH \cdot$	1.1×10^{10}	1.2×10^{10}	1994CHR/SEH527-531
10	$e_{aq}^- + HO_2^- \rightarrow O^{\cdot-} + OH^-$	3.5×10^9	3.5×10^9	1967FEL/GAL384-392
11	$e_{aq}^- + HO_2 \cdot \rightarrow HO_2^-$	2.0×10^{10}	Not found	
12	$e_{aq}^- + O_2 \rightarrow O_2^{\cdot-}$	1.9×10^{10}	1.8×10^{10}	1990ELL/MCC1539-1547
13*	$e_{aq}^- + O_2^{\cdot-} (+H_2O) \rightarrow HO_2^- + OH^-$	1.3×10^{10}	1.3×10^{10}	1971GRU/HEN126-134
14	$H \cdot + H_2O \rightarrow H_2 + OH \cdot$	11	550	1982HAR/GET29-38
15	$H \cdot + H \cdot \rightarrow H_2$	7.8×10^9	5.0×10^9	1990SEH/CHR499-500
16	$H \cdot + OH \cdot \rightarrow H_2O$	7.0×10^9	7.0×10^9	1965THO702-707
17	$H \cdot + OH^- \rightarrow e_{aq}^-$	2.2×10^7	2.5×10^7	1992HAN/BAR4899-4906
18	$H \cdot + H_2O_2 \rightarrow OH \cdot + H_2O$	9.07×10^7	3.6×10^7	1995MEZ/BAR3127-3132
19	$H \cdot + O_2 \rightarrow HO_2 \cdot$	2.1×10^{10}	1.0×10^{10}	1990ELL/MCC1539-1547
20	$H \cdot + O_2 \rightarrow HO_2^-$	1.8×10^{10}	Not found	
21	$H \cdot + HO_2 \cdot \rightarrow H_2O_2$	1.8×10^{10}	2.0×10^{10}	1970FEN/BRY1221-1227
22	$H \cdot + HO_2 \cdot \rightarrow 2OH$	Not included		
23	$OH \cdot + OH \cdot \rightarrow H_2O_2$	3.6×10^9	4.2×10^9	1990ELL/MCC1539-1547
24	$H \cdot + HO_2^- \rightarrow OH + OH^-$	9.0×10^7	1.2×10^9	1995MEZ/BAR3127-3132
25	$OH \cdot + O^{\cdot-} \rightarrow HO_2^-$	2.5×10^{10}	$\leq 2.0 \times 10^{10}$	1966RAB/MAT761-769
26	$OH \cdot + H_2 \rightarrow H \cdot + H_2O$	4.3×10^7	3.4×10^7	1983CHR/SEH118-120
27	$OH \cdot + OH^- \rightarrow O^{\cdot-} + H_2O$	1.3×10^{10}	1.3×10^{10}	1971ZEH/RAB1738-1744
28	$OH \cdot + H_2O_2 \rightarrow H_2O + HO_2 \cdot$	2.7×10^7	2.7×10^7	1988BUX/GRE513-886
29	$OH \cdot + HO_2^- \rightarrow OH^- + HO_2 \cdot$	7.5×10^9	7.5×10^9	1982CHR/SEH1588-1590
30	$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	5.74×10^4	Not found	
31	$OH \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$	6.0×10^9	1.0×10^{10}	1992ELL/BUX2465-2470

No	Reaction	Pastina and LaVerne (2001)	Database	Ref
32	$OH\cdot + O_2^- \rightarrow OH^- + O_2$	8.2×10^9	1.0×10^{10}	1992ELL/BUX2465-2470
33	$O^- + H_2O \rightarrow OH^- + OH\cdot$	1.86×10^6	9.4×10^7	1971ZEH/RAB1738-1744
34*	$O^- + O^- (+H_2O) \rightarrow HO_2^- + OH^-$	1.0×10^9	8.4×10^9	1966ADA/BOA321-341 – not reliable according to database
35	$O^- + H_2 \rightarrow H\cdot + OH^-$	8.0×10^7	1.1×10^8	1991HIC/SEH744-747
36	$O^- + H_2O_2 \rightarrow O_2^- + H_2O$	5.0×10^8	Not found	
37	$O^- + HO_2^- \rightarrow O_2^- + OH^-$	4.0×10^8	4.0×10^8	1988BUX/GRE513-886
38	$O^- + O_2 \rightarrow O_3^-$	3.6×10^9	3.5×10^9	1989ELL/MCC69-74
39	$O^- + O_2^- \rightarrow 2OH^- + O_2$	6.0×10^8	6.0×10^8	1982SEH/HOL2066-2069
40	$H_2O_2 \rightarrow H^+ + HO_2^-$	0.112	Not found	
41	$H^+ + HO_2^- \rightarrow H_2O_2$	5.0×10^{10}	Not found	
42	$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1.3×10^{10}	Not found	
43	$H\cdot \rightarrow e_{aq}^- + H^+$	3.91	Not found	
44	$O^- + H^+ \rightarrow OH\cdot$	1.0×10^{11}	Not found	
45	$HO_2 \rightarrow O_2^- + H^+$	1.35×10^6	Not found	
46	$O_2^- + H^+ \rightarrow HO_2$	5.0×10^{10}	Not found	
47	$HO_2 + OH^- \rightarrow O_2^- + H_2O$	5.0×10^{10}	Not found	
48	$O_2^- + H_2O \rightarrow HO_2 + OH^-$	18.62	Not found	
49	$HO_2 + H_2O \rightarrow O_2^- + H^+$	Not included		
50*	$e_{aq}^- + O_3 (+H_2O) \rightarrow O_2 + 2OH^-$	1.6×10^{10}	Not found	
51	$e_{aq}^- + O_3 \rightarrow O_3^-$	3.6×10^{10}	3.6×10^{10}	1983SEH/HOL1951-1954
52	$H + O_3 \rightarrow O_2 + OH$	Not included		
53	$H\cdot + H_2O \rightarrow H_2 + OH\cdot$	11	550	1982HAR/GET29-38
54	$H\cdot + O^- \rightarrow OH^-$	1.0×10^{10}	Not found	
55	$H\cdot + HO_2^- \rightarrow OH\cdot + OH^-$	9.0×10^7	1.2×10^9	1995MEZ/BAR3127-3132
56	$H\cdot + O_3^- \rightarrow OH^- + O_2$	1.0×10^{10}	Not found	
57	$H\cdot + O_3 \rightarrow HO_3$	3.8×10^{10}	2.2×10^{10}	1983SEH/HOL1951-1954
58	$OH\cdot + O_3^- \rightarrow O_3 + OH^-$	2.6×10^9	Not found	
59	$OH\cdot + O_3^- \rightarrow 2O_2^- + H^+$	6.0×10^9	8.5×10^9	1984SEH/HOL269-273
60	$OH\cdot + O_3 \rightarrow HO_2 + O_2$	1.1×10^8	1.1×10^8	1984SEH/HOL4144-4147
61	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	8.0×10^7	9.7×10^7	1985BIE/CAB1041-1100
62	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	7.0×10^5	1.0×10^6	1988CHR/SEH3007-3011
63	$HO_2 + O^- \rightarrow O_2 + OH^-$	6.0×10^9	Not found	
64	$HO_2 + H_2O_2 \rightarrow OH\cdot + O_2 + H_2O$	0.50	0.50	1979WEI/BIE58-62
65	$HO_2 + HO_2^- \rightarrow OH\cdot + O_2 + OH^-$	0.50	Not found	
66	$HO_2 + O_3^- \rightarrow 2O_2 + OH^-$	6.0×10^9	Not found	
67	$HO_2 + O_3 \rightarrow HO_3 + O_2$	5.0×10^8	Not found	
68*	$2O_2^- (+2H_2O) \rightarrow H_2O_2 + O_2 + OH^-$	100	<0.35	1988CHR/SEH3007-3011
69	$O_2^- + H_2O_2 \rightarrow OH\cdot + O_2 + OH^-$	0.13	0.13	1979WEI/BIE58-62
70	$O_2^- + HO_2^- \rightarrow O\cdot^- + O_2 + OH^-$	0.13	<2	1976MAR7504-7507
71*	$O_2^- + O_3 (+H_2O) \rightarrow 2O_2 + 2OH^-$	1.0×10^4	Not found	
72	$O_2^- + O_3 \rightarrow O_3^- + O_2$	1.5×10^9	1.6×10^9	1984BUE/STA2560-5450
73	$O^- + O_3^- \rightarrow 2O_2^-$	7.0×10^8	7.0×10^8	1982SEH/HOL2066-2069
74	$O^- + O_3 \rightarrow O_2^- + O_2$	5.0×10^9	Not found	
75	$O_3^- \rightarrow O_2 + O^-$	3.3×10^3	2.6×10^3	1989ELL/MCC69-74
76	$O_3^- + H^+ \rightarrow O_2 + OH\cdot$	9.0×10^{10}	9.0×10^{10}	1984SEH/HOL269-273
77	$HO_3 \rightarrow O_2 + OH\cdot$	1.1×10^5	Not found	
78	$O_3 + H_2O \rightarrow O_2 + O^-$	Not included		
79	$OH \rightarrow H^+ + O^-$	0.13	Not found	

* Water is not included in the rate expression for which the rate constant is valid. To convert the rate constant to include also water, the tabulated value should be divided by $[H_2O]$ or $[H_2O]^2$ depending on if there is one or two water molecules among the reactants.

As can be seen, a number of the reactions cannot be found in the database. Most of them are protonation/deprotonation reactions and these reactions are generally not listed in the database. Among the reactions available in the database, the agreement with data in set 1 is quite good which further strengthens the reliability of this dataset. It may be pointed out that rate constants where cross comparison is not possible should be prioritized in future evaluations.

One of the most important groundwater constituents in view of spent nuclear fuel dissolution is bicarbonate/carbonate ($\text{HCO}_3^-/\text{CO}_3^{2-}$). The main reason for this is that carbonate forms complexes with U(VI) and also ternary complexes with U(VI) and H_2O_2 . This has a direct impact on the dissolution but also on the speciation of H_2O_2 . The second reason is that $\text{HCO}_3^-/\text{CO}_3^{2-}$ is quite reactive towards hydroxyl radicals forming $\text{CO}_3^{\cdot-}$. Therefore, the reaction scheme involving bicarbonate/carbonate must also be included. The most comprehensive collection of reactions and rate constants can be found in Cai et al. (2001). The reactions and rate constants are listed in Table 2-4 along with the corresponding values found in the database (NIST Standard Reference Database 40).

Table 2-4. Carbonate reactions.

No	Reaction	Cai et al. (2001)	Database	Ref
80	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}^+$	2.0×10^4	Not found	
81	$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$	5.0×10^{10}	Not found	
82	$\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$	2.0	Not found	
83	$\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$	5.0×10^{10}	Not found	
84	$\text{CO}_2 + e_{\text{aq}}^- \rightarrow \text{CO}_2^-$	7.7×10^9	7.7×10^9	1963GOR/HAR193-205
85	$\text{CO}_3^{2-} + e_{\text{aq}}^- \rightarrow \text{CO}_2^- + 2\text{OH}^-$	3.9×10^5	3.9×10^5	1981NAS/MUL897-899
86	$\text{HCO}_3^- + \text{H} \cdot \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2$	4.4×10^4	4.4×10^4	1963NEH/RAB1609-1613
87	$\text{HCO}_3^- + \text{OH} \cdot \rightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O}$	8.5×10^6	8.5×10^6	1988BUX/GRE513-886
88	$\text{CO}_3^{2-} + \text{OH} \cdot \rightarrow \text{CO}_3^{\cdot-} + \text{OH}^-$	3.9×10^8	3.9×10^8	1988BUX/GRE513-886
89	$2\text{CO}_3^{2-} \rightarrow \text{C}_2\text{O}_6^{2-}$	1.4×10^7	1.4×10^7	1986SAI/BHA189-193
90	$\text{C}_2\text{O}_6^{2-} \rightarrow \text{C}_2\text{O}_4^{2-} + \text{O}_2$	1.0	Not found	
91 ^a	$\text{C}_2\text{O}_6^{2-} + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{OH}^- + 2\text{CO}_2$	2.0×10^2	Not found	
92	$\text{CO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{CO}_3^{\cdot-} + \text{O}_2 + 2\text{H}^+$	9.8×10^5	4.3×10^5	1991DRA/NEG317-321
93	$\text{CO}_3^- + \text{HO}_2^- \rightarrow \text{CO}_3^{\cdot-} + \text{O}_2 + \text{H}^+$	1.0×10^7	1.0×10^7	1983ERI/LIN1493-1501
94	$\text{CO}_3^- + \text{O}_2^- \rightarrow \text{CO}_3^{\cdot-} + \text{O}_2$	4.0×10^8	6.5×10^8	1985ERI/LIN197-199
95	$\text{CO}_3^- + \text{CO}_2^- \rightarrow \text{CO}_3^{\cdot-} + \text{CO}_2$	3.0×10^8	5.0×10^7	1991DRA/NEG317-321
96	$\text{CO}_2^- + e_{\text{aq}}^- \rightarrow \text{HCOO}^- + \text{OH}^-$	1.0×10^9	1.0×10^9	1993ERS/JAN4589-4594
97	$2\text{CO}_2^- \rightarrow \text{C}_2\text{O}_4^{2-}$	6.5×10^8	6.5×10^8	1986MUL/DAN5347-5352
98	$\text{CO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{CO}_2 + \text{OH} \cdot + \text{OH}^-$	7.3×10^5	7.3×10^5	1987KIS/MOO309-313
99	$\text{CO}_2^- + \text{HCO}_3^- \rightarrow \text{CO}_3^{\cdot-} + \text{HCOO}^-$	1.0×10^9	2.0×10^9	1991DRA/NEG317-321
100	$\text{CO}_3^- + \text{HCOO}^- \rightarrow \text{HCO}_3^- + \text{CO}_2^-$	1.5×10^5	1.5×10^5	1991DRA/NEG317-321
101	$\text{OH} \cdot + \text{HCOO}^- \rightarrow \text{CO}_2^- + \text{H}_2\text{O}$	3.2×10^9	3.2×10^9	1993MOT/SAI1842-1845
102	$\text{H} \cdot + \text{HCOO}^- \rightarrow \text{CO}_2^- + \text{H}_2$	2.1×10^8	2.1×10^8	1988BUX/GRE513-886
103	$e_{\text{aq}}^- + \text{HCOO}^- \rightarrow \text{CO}_2^- + \text{H}_2 - \text{H}^+$	8.0×10^3	8.0×10^3	1992SCH8937-8941
104	$\text{OH} \cdot + \text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_2^- + \text{CO}_2 + \text{OH}^-$	7.7×10^6	7.7×10^6	1971GET/SCH749-755
105	$\text{CO}_2^- + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^-$	2.0×10^9	2.0×10^9	1976BUX/SEL1464-1476
106	$\text{CO}_3^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{C}_2\text{O}_4^- + \text{CO}_3^{\cdot-}$	3.0×10^9	Not found	
107	$e_{\text{aq}}^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{C}_2\text{O}_4^{\cdot-}$	3.1×10^7	3.1×10^7	1986MUL/DAN5347-5352

^a 1st order rate constant (s^{-1})

As can be seen, many of the rate constants found in the database are identical to the rate constants from Cai et al. (2001). The reason for this is in some cases that they have the same origin and it is therefore not possible to critically assess the data.

2.4 Recommendations

The general recommendation for the future development and utilization of numerical models describing the dynamics of radiation induced dissolution of spent nuclear fuel is to base the simulation of radiation chemistry of groundwater on the G-values and reaction set with rate constants published by Pastina and LaVerne (2001). The radiation chemistry of bicarbonate/carbonate should be described on the basis of the data presented in Cai et al. (2001).

References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at www.skb.com/publications.

- Buck E C, Wittman R S, Skomurski F N, Cantrell K J, McNamara B K, Soderquist C Z, 2012.** Radiolysis process modeling results for scenarios. FCRD-UFD-2012-000199, PNNL-21554, Pacific Northwest National Laboratory.
- Cai Z, Li X, Katsumura Y, Urabe O, 2001.** Radiolysis of bicarbonate and carbonate aqueous solutions: product analysis and simulation of radiolytic processes. *Nuclear Technology* 136, 231–240.
- Choppin G R, Liljenzin J-O, Rydberg J, 2002.** Radiochemistry and nuclear chemistry. 3rd ed. Woburn, MA: Butterworth-Heinemann.
- Christensen H, Bjergbakke E, 1985.** Alpha-radiolysis of aqueous solutions. *MRS Online Proceedings Library* 50, 401–408.
- Ekeroth E, Roth O, Jonsson M, 2006.** The relative impact of radiolysis products in radiation induced oxidative dissolution of UO_2 . *Journal of Nuclear Materials* 355, 38–46.
- Elliot A J, Bartels D M, 2009.** The reaction set, rate constants and g-values for the simulation of the radiolysis of light water over the range 20° to 350 °C based on information available in 2008. AECL 153-127160-450-001, Atomic Energy of Canada Limited.
- Jonsson M, Nielsen F, Roth O, Ekeroth E, Nilsson S, Hossain M M, 2007.** Radiation induced spent nuclear fuel dissolution under deep repository conditions. *Environmental Science & Technology* 41, 7087–7093.
- Meesungnoen J, Jay-Gerin J-P, 2010.** Radiation chemistry of liquid water with heavy ions: Monte Carlo simulation studies in charged particle and photon interactions with matter – Recent advances, applications, and interfaces. In Hatano Y, Katsumura Y, Mozumber A (eds). *Charged particle and photon interactions with matter*. Boca Raton, FL: CRC Press, 355-400.
- Mozumber A, 1999.** Fundamentals of radiation chemistry. London: Academic Press.
- Pastina B, LaVerne J A, 2001.** Effect of molecular hydrogen on hydrogen peroxide in water radiolysis. *The Journal of Physical Chemistry A* 105, 9316–9322.
- Poinsot C, Ferry C, Kelm M, Grambow B, Martinez A, Johnson L, Andriambololona Z, Bruno J, Cachoir C, Cavedon J M, Christensen H, Corbel C, Jegou C, Lemmens K, Loida A, Lovera P, Miserque F, De Pablo J, Poulesquen A, Quinones J, Rondinella V, Spahiu K, Wegen D H, 2004.** Spent fuel stability under repository conditions – Final report of the European Project. Contract No FIKW-CT-2001-00192 SFS. European Commission, 5th Euratom Framework Programme 1998–2002.
- Shoosmith D W, 2000.** Fuel corrosion under waste disposal conditions. *Journal of Nuclear Materials* 282, 1–31.

SKB is responsible for managing spent nuclear fuel and radioactive waste produced by the Swedish nuclear power plants such that man and the environment are protected in the near and distant future.

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