# MONTE-CARLO SIMULATION OF THE RADIOLYSIS OF SUPERCRITICAL WATER AT 400 °C AND LIQUID-LIKE DENSITIES

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## Abstract

Monte-Carlo simulations are used to calculate the primary radical yields $g(e^-_{aq})$, $g(^{\bullet}OH)$, the sum $[g(e^-_{aq}) + g(^{\bullet}OH) + g(H^{\bullet})]$, and the ratio $g(H^{\bullet})/g(e^-_{aq})$ in the low-LET radiolysis of supercritical water (SCW) at 400 °C in the high-density, liquid-like region near ~0.5 g/cm$^3$. Using all the currently available information on the reactivities and diffusion coefficients of the radiation-induced species under these conditions, a good accord is found between the calculated and the available experimental yield values. In particular, our computed $e^-_{aq}$ yields at 60 ps and 1 ns compare very well with the recently reported time-dependent yields of hydrated electrons in SCW at 400 ºC.

## 1. Introduction

While experiments showing that water is decomposed by X rays and radium date back to the early 20th century, various quantitative aspects of this radiolysis are not yet fully resolved [1-3]. This is particularly true in water-cooled nuclear reactors which use water as heat transfer medium, neutron moderator, and shield [4]. Current, state-of-the-art pressurized water reactors operate at ~250-330 °C and 10 MPa pressure. They essentially provide a source of heat used to drive a "heat engine" (turbine) to generate electricity. Based on the second law of thermodynamics, an obvious way to increase the operating efficiency and profitability of future nuclear power plants is to heat the water of the primary circuit to even higher temperatures. Fourth-generation nuclear technology (Gen IV) designs under consideration [5-10] would operate at ~430-625 °C and 25 MPa, *i.e.*, well beyond the thermodynamic critical point of water ($H_2O$: $t_c$ = 373.95 °C, $P_c$ = 22.06 MPa or 217.7 atm, $\rho_c$ = 0.322 g/cm$^3$/$D_2O$: $t_c$ = 370.74 ºC, $P_c$ = 21.67 MPa or 213.9 atm, $\rho_c$ = 0.358 g/cm$^3$) [11]. Supercritical (light/heavy) water (SCW)-cooled reactors would enable thermodynamic cycle efficiencies as high as ~44% (versus ~33% for existing water reactors), thus generating lower-cost electricity.

An enhanced, reliable understanding of the effects of radiation on aqueous systems in both current water reactors and SCW-cooled nuclear reactors in the future is required in order to specify chemistry control strategies that minimize unwanted corrosion and degradation of components in the reactor circuits resulting from the radiolytic formation of oxidizing products, such as $^{\bullet}OH$, $H_2O_2$, $O_2$, and $O_2^{\bullet -}$ (or $HO_2^{\bullet}$ depending on the pH) [8-10,12]. These products are highly reactive at the elevated temperatures corresponding to normal operating conditions. In current reactor designs, one commonly used remedial measure to chemically prevent the net radiolytic production of oxidizing species in the water is to add a small overpressure of excess $H_2$ in the reactor coolant. It is still unclear, however, whether this "hydrogen water chemistry", or some variant on the same theme, would also be effective under SCW conditions [9]. Moreover, the water in reactor cores is subject not only to extreme conditions of high temperature and pressure, but also to an intense flux of ionizing radiations (fast neutrons, $\gamma$-rays, recoil protons and heavy ions), which are the main source of the troublesome oxidizing products [9,10,13,14]; for these reasons, its radiolysis is difficult to determine experimentally.

As experiments at very high temperatures and pressures, and especially beyond the critical point of water, are difficult to perform, theoretical models and computer simulations of the radiation chemistry of the cooling water are an important route of investigation [9,10,14,15]. However, a large amount of input information on the reaction rate constants ($k$) of radiation-induced species, reaction mechanisms, diffusion coefficients ($D$), and radiolytic yields (or $g$-values) in subcritical water and in the SCW regime is needed in order to create such models. This information is important since preliminary studies suggest, in many cases, a markedly different behavior of the effects of radiation at SCW conditions compared to what one would predict from simplistic extrapolations of experimental data originally measured at lower temperatures. Key examples here include the rate constants of a growing number of chemical reactions that are found to exhibit, at elevated temperatures, negative Arrhenius activation energies (*i.e.*, the temperature dependence of $k$ actually decreases gradually with temperature above a certain temperature), so that earlier attempts to extrapolate existing experimental data on reactivities from their measured ranges (mostly less than 250-310 °C [15-18]) to the temperatures of interest, assuming simple Arrhenius behavior, should be viewed with caution [9,19-24]. Since about 2000, there has been a revival in the study of the high-temperature radiolysis of water due, in large part, to the need for information on SCW. Generally, these studies have been able to extend the measurements of both reaction rates and $g$-values to higher temperatures than the original investigations, thereby reducing or, in some cases, eliminating the need to extrapolate the data (for a recent compilation and critical review of radiolysis data up to 350 ºC, see [24]). More recently, the need to model chemistry in a SCW-cooled reactor has initiated concerted national and international experimental programs that are now underway in several laboratories to generate the necessary radiation chemistry data. Currently, however, only limited experimental data are available on the radiation chemistry and reaction kinetics of transients in SCW [8,9,13,19,20,25-34].

The present work is a first attempt to extend our previous Monte-Carlo track structure simulations in liquid water at high temperatures [35] to the study of the low linear energy transfer (LET) radiolysis of SCW ($H_2O$) at 400 °C. It represents an initial effort to obtain data to help elucidate mechanisms by which radiation interacts with water in its supercritical regime. The calculations reported herein incorporate all the currently available information on the temperature-dependent reactivities and diffusion coefficients of the radiolytically-produced free radicals and molecular products [$e^-_{aq}$, $H^+$, $OH^-$, $H^\bullet$, $H_2$, $^\bullet OH$, $H_2O_2$, $O_2^{\bullet -}$ (or $HO_2^\bullet$), etc.] [1,36-38] and on the physicochemical properties of water at this temperature. To our knowledge, no theoretical modeling of the radiolysis of water at such elevated temperatures has been reported so far. Even if uncertainties abound throughout, we have used parameters which appear reasonable to us. Rather than waiting until better data become available, our first objective here is to push the calculation all the way to the point that we can compare calculated $g$-values for radiolysis yields with existing experimental observations. Of course, the final objective is a track model which agrees with experimental chemical data.

## 2. Monte-Carlo simulations

The radiolysis of SCW has been modeled using an extended version of our Monte-Carlo track structure simulation code called IONLYS-IRT, which simulates irradiations (by high-energy protons or heavier ions) of pure liquid water or (dilute) aqueous solutions at ambient [39-41] and elevated [35] temperatures. A detailed description of our simulation methodology and reaction scheme can be found in the references cited.

In brief, the IONLYS program models, on an event by event basis, all the events of the early physical ($<10^{-15}$ s) and physicochemical ($\sim10^{-15}$-$10^{-12}$ s) stages [42] in the track development. The complex spatial distribution of reactants present at the end of the physicochemical stage, which is provided as an output of the IONLYS program, is then used directly as the starting point for the subsequent nonhomogeneous chemical stage [42]. This third and final stage ($\sim10^{-12}$-$10^{-6}$ s at room temperature), during which the various radiolytic species diffuse randomly and react with one another (or with available solutes) until all spur/track processes are complete, is covered by our IRT program. This program employs the "independent reaction times" (IRT) method [43,44], a computer efficient stochastic simulation technique that is used to simulate reaction times without having to follow the trajectories of the diffusing species. The IRT method relies on the approximation that the reaction time for each pair of reactants is independent of the presence of other reactants in the system. Such an approximation has been found to be accurate in solvents of high dielectric constant, where the Coulomb forces between the ions are weak (as is the case with ordinary water), but the method has also been used in intermediate and low-permittivity solvents (such as water at elevated temperatures, alcohols, and hydrocarbons) [35,45-47]. Within the framework of this approach, the competition between the reactions is simply described via a sorting out of the stochastically sampled reaction times for each of the potentially reactive pairs of reactants. The implementation of this program has been described previously [40,41] and its ability to give accurate time-dependent chemical yields has been well validated by comparison with full random flight Monte-Carlo simulations that do follow the reactant trajectories in detail [44,48,49].

In the present version of IONLYS-IRT, the rate constants of the dominant chemical and acid/base equilibrium reactions involved in the radiolysis of SCW at 400 °C in the liquid-like region studied have usually been obtained by extrapolating the experimental data recently compiled by Elliot and Bartels [24] from their measured ranges (mostly 20-350 °C). In some cases, the kinetic data of Ghandi and Percival [20] inferred from muon spin spectroscopy measurements in subcritical water and SCW (up to 450 ºC) have also been used. The corresponding $k$ values employed in our simulations are listed in Table 1.

Note the particular case of the self-reaction of $e^-_{aq}$ (reaction R10) whose temperature dependence is still a subject of questioning [23,24] that requires some clarification. Its rate constant has been chosen here by following the extrapolation procedure previously proposed by Elliot [16], and employed in [35], which consists to assume that this reaction is diffusion-controlled above 150 ºC. The validity of this assumption is confirmed by the good agreement of the calculated and experimental $g(e^-_{aq})$ values up to 350 ºC (data not shown). In contrast, if the abrupt decrease in this rate constant observed in alkaline solution above 150 ºC is included in our simulations, a sharp downward discontinuity in $g(H_2)$ is predicted [35,51,52], which is not observed experimentally [24]. This abrupt drop needs to be confirmed in near-neutral solution, as it may be a function of the pH of the solution [16-18].

Table 1 Main spur/track reactions and values at 400 °C for the corresponding rate constants ($k$) used in our simulations.

| Symbol | Reaction | $k$ ($10^{10}$ $M^{-1}$ $s^{-1}$) |
|---|---|---|
| R1 | $^{\bullet}OH + e^{-}_{aq} \rightarrow OH^{-}$ | 45 [a] |
| R2 | $^{\bullet}OH + H^{\bullet} \rightarrow H_2O$ | 4.4 [b] |
| R3 | $^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$ | 0.85 [a] |
| R4 | $^{\bullet}OH + HO_2^{\bullet} \rightarrow O_2 + H_2O$ | 3 [a] |
| R5 | $^{\bullet}OH + H_2 \rightarrow H^{\bullet} + H_2O$ | 0.06 [a] |
| R6 | $e^{-}_{aq} + H^{+} \rightarrow H^{\bullet}$ | 300 [a,c] |
| R7 | $e^{-}_{aq} + H^{\bullet} \rightarrow H_2 + OH^{-}$ | 79 [a] |
| R8 | $H^{\bullet} + OH^{-} \rightarrow e^{-}_{aq} + H_2O$ | 2.2 [a] |
| R9 | $H^{+} + OH^{-} \rightarrow H_2O$ | 200 [a] |
| R10 | $e^{-}_{aq} + e^{-}_{aq} \rightarrow H_2 + 2\ OH^{-}$ | 21 [d] |
| R11 | $H^{\bullet} + H^{\bullet} \rightarrow H_2$ | 15 [e] |
| R12 | $H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$ | 6.7 [a] |
| R13 | $H^{\bullet} + HO_2^{\bullet} \rightarrow 2\ {}^{\bullet}OH$ | 34 [a] |
| R14 | $H^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O$ | 0.23 [a] |
| R15 | $e^{-}_{aq} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^{-}$ | 46 [a] |
| R16 | $^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$ | 0.06 [a] |
| R17 | $e^{-}_{aq} + O_2 \rightarrow O_2^{\bullet -}$ | 25 [a,f] |

[a] Extrapolated from [24].
[b] From Fig. 2 of [20]. See also [24].
[c] See also [50].
[d] Extrapolated from Fig. 3 of [16], assuming reaction R10 is diffusion controlled and using the experimental data up to 150 °C. See also [35].
[e] Extrapolated from Fig. 7 of [16], assuming reaction R11 is diffusion controlled. See also [24].
[f] See also [27].

For the other reactions, whose rate constants have been measured only up to 200 or 250 °C (many of these data have been collected and summarized in [15-18,24] for both $H_2O$ and $D_2O$), the available data for $k$ have been extrapolated above their experimentally studied temperature range as described previously [35]. Due to the lack of experimental data, we have simply chosen to neglect any dependence of the reaction rate constants on water density on the 400 °C isotherm; this approximation should not be too severe, if one considers the limited range of densities investigated here.

The diffusion coefficients used for the main reactive species are listed in Table 2. The values of the viscosity ($\eta \sim 58.6$ μPa.s), static dielectric constant ($\varepsilon_0 \sim 9.6$), and molar concentration

(~27.8 *M*) of SCW at 400 °C and ~0.5 g/cm$^3$ have been taken from the NIST Chemistry WebBook [11], whereas the ionic product of water ($K_w$) has been obtained from Bandura and Lvov [56]. Finally,

Table 2 Values at 400 °C for the diffusion coefficients (*D*) of reactive species in SCW in the high-density region around ~0.5 g/cm$^3$.

| Species | $D$ ($10^{-9}$ m$^2$ s$^{-1}$) |
|---|---|
| $H_2$ [a] | 146 |
| $H_2O_2$ [a] | 70 |
| $H^\bullet$ [a] | 213 |
| $^\bullet OH$ [a] | 67 |
| $e^-_{aq}$ | 420 [b] |
| $H_3O^+$ | 56 [c] |
| $OH^-$ | 58 [c] |
| $H_2O$ [a] | 70 |

[a] The diffusion coefficients of $H_2$, $H_2O_2$, $H^\bullet$, and $^\bullet OH$, explicitly determined at 25 °C but essentially unknown at 400 °C, are assumed to scale according to the self-diffusion of water [16-18,23,35,51]. The values of *D* at 25 °C for the various reactants are taken from [16,35]. $D_{H_2O}(25\ °C) = 2.299 \times 10^{-9}$ m$^2$ s$^{-1}$ [53]. The self-diffusion coefficient of compressed SCW at 400 °C and ~0.5 g/cm$^3$ is taken to be $70 \times 10^{-9}$ m$^2$ s$^{-1}$ from the measurements of Lamb *et al.* [54].
[b] Extrapolated from the data of Schmidt *et al.* [55] up to 90 °C and the estimate of Marin *et al.* [23] at 300 °C (~$240 \times 10^{-9}$ m$^2$ s$^{-1}$).
[c] Obtained by extrapolation of the experimental data reported by Elliot and Bartels (Fig. 4-27 of [24]) over the 0-350 °C temperature range.

from a microscopic viewpoint, we have ignored here the heterogeneous structural characteristics of SCW originating from the existence of density fluctuations (or water "clustering") that are associated with the high compressibility of water in the vicinity of $t_c$ [57-61]. In our simulations, we assume that the overall instantaneous picture of SCW can simply be viewed as a *continuum* medium with mean density equal to the density of bulk water. This approximation is thought to be reasonable at the liquid-like SCW densities considered in this study [58,60] and it seems to be justified by the agreement we have obtained between model and experiment (see below).

To reproduce the effects of $^{60}$Co γ-rays or fast electrons, we use short (~100-μm) segments of ~300-MeV proton tracks, over which the LET is essentially constant and equal to ~0.3 keV/μm in normal liquid water at 25 °C. Such an analysis thus gives "track segment" yields [62] as a function of time from picoseconds to microseconds. The number of proton histories (~150) is chosen so as to ensure only small statistical fluctuations when calculating average yields, while keeping acceptable computer time limits.

## 3. Results and discussion

Table 3 compares our calculated values of $g(e^-_{aq})$, $g(^\bullet OH)$, the sum $[g(e^-_{aq}) + g(^\bullet OH) + g(H^\bullet)]$, and the ratio $g(H^\bullet)/g(e^-_{aq})$ with available experimental data [30,32-34] for the low-LET radiolysis of pure, deaerated SCW at 400 °C and ~0.5 g/cm$^3$. As we can see, a good overall agreement is obtained between experiment and theory.

Table 3 Comparison of available experimental data (in molecule/100 eV) of $g(e^-_{aq})$, $g(^\bullet OH)$, $[g(e^-_{aq}) + g(^\bullet OH) + g(H^\bullet)]$, and $g(H^\bullet)/g(e^-_{aq})$ in the low-LET radiolysis of SCW at 400 °C and in the liquid-like region around ~0.5 g/cm$^3$ with the results of our Monte-Carlo simulations.[a]

| Yield | Experiment | This work [b] |
|---|---|---|
| $g(e^-_{aq})$ | | |
| | 3.48 ± 0.2 [c] at 0.570 g/cm$^3$ and ~60 ps [34] | 3.15 at 60 ps |
| | 2.46 ± 0.2 [c] at 0.570 g/cm$^3$ and ~1 ns [34] | 2.55 at 1 ns |
| | 2.29 at 0.523 g/cm$^3$ [30] | |
| | 2.36 at 0.502 g/cm$^3$ [30] | 2.26 |
| | 2.45 [d] at 0.475 g/cm$^3$ [30] | |
| $g(e^-_{aq}) + g(^\bullet OH) + g(H^\bullet)$ | | |
| | 9.45 at 0.523 g/cm$^3$ [30] | |
| | 9.35 at 0.502 g/cm$^3$ [30] | 9.07 |
| | 9.55 at 0.475 g/cm$^3$ [30] | |
| | 9.38 at 0.523 g/cm$^3$ [33] | |
| | 10.08 at 0.475 g/cm$^3$ [33] | |
| $g(^\bullet OH)$ | | |
| | 5.41 [e] at 0.523 g/cm$^3$ [32] | 4.91 |
| | 5.63 [e] at 0.475 g/cm$^3$ [32] | |
| $g(H^\bullet)/g(e^-_{aq})$ | | |
| | 0.996 [f] at 0.523 g/cm$^3$ | 0.84 |
| | 1.11 [f] at 0.475 g/cm$^3$ | |

[a] Most data reported here are derived from scavenged yields of species measured in steady-state experiments and supposed ideally to be close to the "escape" yields from the spur [24,37,62]. Unless otherwise indicated, our calculated yields are all obtained assuming a scavenging time of ~10 ns [13].

[b] All yield values are computed for a SCW density of 0.5 g/cm$^3$.

[c] Direct observation using picosecond pulse radiolysis experiments in supercritical $D_2O$.

[d] Janik *et al.* [13] also reported the $e^-_{aq}$ escape yields in SCW at 380 and 400 °C as a function of density using $N_2O$ as a specific scavenger for $e^-_{aq}$ (rather than the *tert*-BuOH/methyl viologen scavenging system used in the experiments of Lin *et al.* [30]). At their highest densities studied (~0.42-0.55 g/cm$^3$), their $e^-_{aq}$ yields are comparable with those measured by Lin *et al.* [30].

[e] Average over several determinations.

[f] Obtained from the product yield measurements without considering the scavenging time for the two species (M. Lin, personal communication, 2008). Similar values of this ratio have also been reported at 380 °C in the density regime studied here by Janik *et al.* [13] (see also [27]).

Let us note briefly here the three following points. First, there is currently only very limited information on the yields of water radiolysis products under supercritical conditions. In fact, published data mainly concern *g*-values for $e^-_{aq}$ [9,13,25-27,30,31,34], $H^\bullet$ atom [9,13,27], $H_2$ [9,13], and $^\bullet OH$ [32] production in low-LET radiolysis up to 400 °C. Most of these studies employ steady-state radiolysis experiments with various specific scavengers, assuming that they (and the products formed) are thermally stable in SCW. However, because of the lack of precise determination of the rate constants for the reactions between radicals and scavengers, the scavenging time (*i.e.*, reciprocal of the "scavenging power", defined as the product of *k* and the scavenger concentration) corresponding to the *g*-values reported at high temperature is not well known and may differ depending on the considered experimental conditions. In the calculations reported in Table 3, we have assumed that the scavenging time in those yield experiments is ~10 ns [13]. Second, as shown in Table 3, there is a good agreement between our computed $e^-_{aq}$ yields at 60 ps and 1 ns and the corresponding *g*-values measured in SCW ($D_2O$) by Muroya *et al.* [34] using picosecond pulse radiolysis experiments. In this context, it is remarkable to note that these *direct* time-dependent $e^-_{aq}$ yield measurements [34] compare very well with Lin et al.'s previous studies [30,31] that used scavenging methods. Finally, our third point concerns the importance of the charge-recombination reaction R6 (see Table 1) in irradiated SCW at 400 °C. In fact, the rate constant for this reaction is known only up to 350 °C [24,50]. However, in light of the recent measurements of Muroya *et al.* [34], which appear to indicate that reaction R6 at 400 °C is even faster than that at 350 °C, we have determined the sensitivity of our simulated radiolytic yields on variations in the value of the rate constant for this reaction. As expected [13,34], reaction R6 has a major impact on the calculated yields of $g(e^-_{aq})$ and $g(H^\bullet)$. For example, at 400 °C and 0.5 g/cm$^3$, the ratio $g(H^\bullet)/g(e^-_{aq})$ at 10 ns varies from 0.74 to 1.26 molecule/100 eV when the rate constant is varied from 2.5 to 5 × $10^{12}$ $M^{-1}$ $s^{-1}$. By contrast, $g(^\bullet OH)$ and $g(H_2)$ are found to be rather insensitive to this parameter.

## 4. Conclusion

In this work, we have presented, in the light of the available experimental data, the results of our calculated yields of the free radical products $e^-_{aq}$, $^\bullet OH$ radical, and $H^\bullet$ atom, in irradiated SCW at 400 °C and liquid-like densities around ~0.5 g/cm$^3$. The good overall accord between experiment and theory shows that Monte-Carlo simulations offer a most promising avenue at present to further develop our understanding of temperature/pressure (density) effects in the radiolysis of SCW under various thermodynamic conditions. Currently, work is in progress at our laboratory to calculate the *g*-values in SCW at 400 °C in the low-density, gas-like region near ~0.15 g/cm$^3$.

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## 6. References

[1] C. Ferradini and J.-P. Jay-Gerin, "La radiolyse de l'eau et des solutions aqueuses: historique et actualité", *Canadian Journal of Chemistry*, Vol. 77, 1999, pp. 1542-1575.

[2] "Research needs and opportunities in radiation chemistry workshop", Report DOE/SC-0003, U.S. Department of Energy, Germantown, MD, 1999.

[3] B.C. Garrett *et al.* (46 authors), "Role of water in electron-initiated processes and radical chemistry: Issues and scientific advances", *Chemical Reviews*, Vol. 105, 2005, pp. 355-390.

[4] P. Cohen, *Water Coolant Technology of Power Reactors*, American Nuclear Society, La Grange Park, IL, 1980.

[5] Y. Oka and S. Koshizuka, "Conceptual design study of advanced power reactors", *Progress in Nuclear Energy*, Vol. 32, 1998, pp. 163-177.

[6] "A technology roadmap for Generation IV nuclear energy systems", Report GIF-002-00, U.S. DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum, Washington, DC, 2002.

[7] H.F. Khartabil, R.B. Duffey, N. Spinks, and W. Diamond, "The pressure-tube concept of Generation IV supercritical water-cooled reactor (SCWR): Overview and status", Proceedings of the International Congress on Advances in Nuclear Power Plants, Seoul, Korea, May 15-19, 2005, Paper 5564.

[8] Y. Katsumura, "Application of radiation chemistry to nuclear technology", *Charged Particle and Photon Interactions with Matter: Chemical, Physical, and Biological Consequences with Applications* (A. Mozumder and Y. Hatano, Eds.), Marcel Dekker, New York, 2004, pp. 697-727.

[9] D.M. Bartels, M. Anderson, P. Wilson, T. Allen, and K. Sridharan, "Supercritical water radiolysis chemistry. Supercritical water corrosion" (material available via the Internet at http://nuclear.inl.gov/deliverables/docs/uwnd_scw_level_ii_sep_2006_v3.pdf).

[10] D. Guzonas, P. Tremaine, and J.-P. Jay-Gerin, "Chemistry control challenges in a supercritical water-cooled reactor", *PowerPlant Chemistry*, Vol. 11, 2009, pp. 284-291.

[11] P.J. Linstrom and W.G. Mallard (*Editors*), *NIST Chemistry WebBook*, NIST Standard Reference Database No. 69, National Institute of Standards and Technology, Gaithersburg, MD, 2005.

[12] G.S. Was *et al.* (11 authors), "Corrosion and stress corrosion cracking in supercritical water", *Journal of Nuclear Materials*, Vol. 371, 2007, pp. 176-201.

[13] D. Janik, I. Janik, and D.M. Bartels, "Neutron and β/γ radiolysis of water up to supercritical conditions. 1. β/γ Yields for $H_2$, $H^•$ atom, and hydrated electron", *Journal of Physical Chemistry A*, Vol. 111, 2007, pp. 7777-7786.

[14] D.R. McCracken, K.T. Tsang, and P.J. Laughton, "Aspects of the physics and chemistry of water radiolysis by fast neutrons and fast electrons in nuclear reactors", Report AECL-11895, Atomic Energy of Canada Ltd., Chalk River, ON, 1998.

[15] H. Christensen, "Fundamental aspects of water coolant radiolysis", SKI Report 2006:16, Swedish Nuclear Power Inspectorate, Stockholm, Sweden, 2006.

[16] A.J. Elliot, "Rate constants and *g*-values for the simulation of the radiolysis of light water over the range 0-300 °C", Report AECL-11073, Atomic Energy of Canada Ltd., Chalk River, ON, 1994.

[17] A.J. Elliot, D.C. Ouellette, and C.R. Stuart, "The temperature dependence of the rate constants and yields for the simulation of the radiolysis of heavy water", Report AECL-11658, Atomic Energy of Canada Ltd., Chalk River, ON, 1996.

[18] C.R. Stuart, D.C. Ouellette, and A.J. Elliot, "Pulse radiolysis studies of liquid heavy water at temperatures up to 250 °C", Report AECL-12107, Atomic Energy of Canada Ltd., Chalk River, ON, 2002.

[19] P.W. Percival, J.-Cl. Brodovitch, K. Ghandi, B.M. McCollum, and I. McKenzie, "H atom kinetics in superheated water studied by muon spin spectroscopy", *Radiation Physics and Chemistry*, Vol. 76, 2007, pp. 1231-1235, and references therein.

[20] K. Ghandi and P.W. Percival, "Prediction of rate constants for reactions of the hydroxyl radical in water at high temperatures and pressures", *Journal of Physical Chemistry A*, Vol. 107, 2003, pp. 3005-3008.

[21] I. Janik, D.M. Bartels, T.W. Marin, and C.D. Jonah, "Reaction of $O_2$ with the hydrogen atom in water up to 350 °C", *Journal of Physical Chemistry A*, Vol. 111, 2007, pp. 79-88.

[22] I. Janik, D.M. Bartels, and C.D. Jonah, "Hydroxyl radical self-recombination reaction and absorption spectrum in water up to 350 °C", *Journal of Physical Chemistry A*, Vol. 111, 2007, pp. 1835-1843.

[23] T.W. Marin, K. Takahashi, C.D. Jonah, S.D. Chemerisov, and D.M. Bartels, "Recombination of the hydrated electron at high temperature and pressure in hydrogenated alkaline water", *Journal of Physical Chemistry A*, Vol. 111, 2007, pp. 11540-11551.

[24] A.J. Elliot and D.M. Bartels, "The reaction set, rate constants and *g*-values for the simulation of the radiolysis of light water over the range 20 to 350 ºC based on information available in 2008", Report AECL-153-127160-450-001, Atomic Energy of Canada Ltd., Chalk River, ON, 2009.

[25] W.G. Burns and W.R. Marsh, "Radiation chemistry of high-temperature (300-410 °C) water", *Journal of the Chemical Society, Faraday Transactions 1*, Vol. 77, 1981, pp. 197-215.

[26] H.E. Sims, "Yields of radiolysis products from γ-irradiated supercritical water – A re-analysis data by W.G. Burns and W.R. Marsh", *Radiation Physics and Chemistry*, Vol. 75, 2006, pp. 1047-1050.

[27] J. Cline, K. Takahashi, T.W. Marin, C.D. Jonah, and D.M. Bartels, "Pulse radiolysis of supercritical water. 1. Reactions between hydrophobic and anionic species", *Journal of Physical Chemistry A*, Vol. 106, 2002, pp. 12260-12269.

[28] K. Takahashi, D.M. Bartels, J.A. Cline, and C.D. Jonah, "Reaction rates of the hydrated electron with $NO_2^-$, $NO_3^-$, and hydronium ions as a function of temperature from 125 to 380 °C", *Chemical Physics Letters*, Vol. 357, 2002, pp. 358-364.

[29] Y. Katsumura (*Editor*), Proceedings of the Workshop on Radiation Effects on Water Chemistry of Supercritical Water-Cooled Reactor, University of Tokyo, Japan, 18-19 September 2003. 156 pp.

[30] M. Lin, Y. Katsumura, Y. Muroya, H. He, G. Wu, Z. Han, T. Miyazaki, and H. Kudo, "Pulse radiolysis study on the estimation of radiolytic yields of water decomposition products in high-temperature and supercritical water: Use of methyl viologen as a scavenger", *Journal of Physical Chemistry A*, Vol. 108, 2004, pp. 8287-8295.

[31] M. Lin, Y. Katsumura, H. He, Y. Muroya, Z. Han, T. Miyazaki, and H. Kudo, "Pulse radiolysis of 4,4'-bipyridyl aqueous solutions at elevated temperatures: Spectral changes and reaction kinetics up to 400 °C", *Journal of Physical Chemistry A*, Vol. 109, 2005, pp. 2847-2854.

[32] M. Lin, Y. Katsumura, Y. Muroya, and Z. Han, "On the yield of OH radical at elevated temperature and supercritical water", Program and Abstracts, Seventh International Symposium on Advanced Science Research on Charged Particle and Photon Interactions with Matter, Tokai, Ibaraki, Japan, 6-9 November 2007, Paper OR41.

[33] M. Lin, Y. Katsumura, Y. Muroya, H. He, T. Miyazaki, and D. Hiroishi, "Pulse radiolysis of sodium formate aqueous solution up to 400 °C: Absorption spectra, kinetics and yield of carboxyl radical $CO_2^{\bullet -}$", *Radiation Physics and Chemistry*, Vol. 77, 2008, pp. 1208-1212.

[34] Y. Muroya, M. Lin, V. de Waele, Y. Hatano, Y. Katsumura, and M. Mostafavi, "First observation of picosecond kinetics of hydrated electrons in supercritical water", *Journal of Physical Chemistry Letters*, Vol. 1, 2010, pp. 331-335; M. Lin, personal communication.

[35] M.-A. Hervé du Penhoat, T. Goulet, Y. Frongillo, M.-J. Fraser, Ph. Bernat, and J.-P. Jay-Gerin, "Radiolysis of liquid water at temperatures up to 300 °C: A Monte-Carlo simulation study", *Journal of Physical Chemistry A*, Vol. 104, 2000, pp. 11757-11770.

[36] A.O. Allen, *The Radiation Chemistry of Water and Aqueous Solutions*, D. Van Nostrand Co., Princeton, N.J., 1961.

[37] J.W.T. Spinks and R.J. Woods, *An Introduction to Radiation Chemistry*, 3rd ed., Wiley, New York, 1990.

[38] G.V. Buxton, "The radiation chemistry of liquid water: Principles and applications", *Charged Particle and Photon Interactions with Matter: Chemical, Physical, and Biological Consequences with Applications* (A. Mozumder and Y. Hatano, Eds.), Marcel Dekker, New York, 2004, pp. 331-363.

[39] V. Cobut, Y. Frongillo, J.P. Patau, T. Goulet, M.-J. Fraser, and J.-P. Jay-Gerin, "Monte Carlo simulation of fast electron and proton tracks in liquid water. I. Physical and physicochemical aspects", *Radiation Physics and Chemistry*, Vol. 51, 1998, pp. 229-243.

[40] Y. Frongillo, T. Goulet, M.-J. Fraser, V. Cobut, J.P. Patau, and J.-P. Jay-Gerin, "Monte Carlo simulation of fast electron and proton tracks in liquid water. II. Nonhomogeneous chemistry", *Radiation Physics and Chemistry*, Vol. 51, 1998, pp. 245-254.

[41] J. Meesungnoen and J.-P. Jay-Gerin, "High-LET radiolysis of liquid water with $^{1}H^{+}$, $^{4}He^{2+}$, $^{12}C^{6+}$, and $^{20}Ne^{9+}$ ions: Effects of multiple ionization", *Journal of Physical Chemistry A*, Vol. 109, 2005, pp. 6406-6419, and references therein.

[42] R.L. Platzman, "The physical and chemical basis of mechanisms in radiation biology", *Radiation Biology and Medicine. Selected Reviews in the Life Sciences* (W.D. Claus, Ed.), Addison-Wesley, Reading, MA, 1958, pp. 15-72.

[43] P. Clifford, N.J.B. Green, M.J. Oldfield, M.J. Pilling, and S.M. Pimblott, "Stochastic models of multi-species kinetics in radiation-induced spurs", *Journal of the Chemical Society, Faraday Transactions 1*, Vol. 82, 1986, pp. 2673-2689.

[44] S.M. Pimblott, M.J. Pilling, and N.J.B. Green, "Stochastic models of spur kinetics in water", *Radiation Physics and Chemistry*, Vol. 37, 1991, pp. 377-388.

[45] M. Běgusová and S.M. Pimblott, "Stochastic simulation of gamma radiolysis of acidic ferrous sulphate solution at elevated temperatures", *Radiation Protection Dosimetry*, Vol. 99, 2002, pp. 73-76.

[46] N.J.B. Green, M.J. Pilling, S.M. Pimblott, and P. Clifford, "Stochastic models of diffusion-controlled ionic reactions-induced spurs. 2. Low-permittivity solvents", *Journal of Physical Chemistry*, Vol. 93, 1989, pp. 8025-8031.

[47] S.M. Pimblott and N.J.B. Green, "Recent advances in the kinetics of radiolytic processes", *Research in Chemical Kinetics*, Vol. 3, 1995, pp. 117-174.

[48] T. Goulet, M.-J. Fraser, Y. Frongillo, and J.-P. Jay-Gerin, "On the validity of the independent reaction times approximation for the description of the nonhomogeneous kinetics of liquid water radiolysis", *Radiation Physics and Chemistry*, Vol. 51, 1998, pp. 85-91.

[49] I. Plante, “Développement de codes de simulation Monte-Carlo de la radiolyse de l’eau par des électrons, ions lourds, photons et neutrons. Applications à divers sujets d’intérêt expérimental”, Ph.D. Thesis, Université de Sherbrooke, Sherbrooke, QC, 2009.

[50] C.M. Stanisky, D.M. Bartels, and K. Takahashi, “Rate constants for the reaction of hydronium ions with hydrated electrons up to 350 °C”, *Radiation Physics and Chemistry*, Vol. 79, 2010, pp. 64-65.

[51] J.A. LaVerne and S.M. Pimblott, “Diffusion-kinetic modeling of the electron radiolysis of water at elevated temperatures”, *Journal of Physical Chemistry*, Vol. 97, 1993, pp. 3291-3297.

[52] D. Swiatla-Wojcik and G.V. Buxton, “Modeling of radiation spur processes in water at temperatures up to 300 °C”, *Journal of Physical Chemistry*, Vol. 99, 1995, pp. 11464-11471.

[53] R. Mills, “Self-diffusion in normal and heavy water in the range 1-45°”, *Journal of Physical Chemistry*, Vol. 77, 1973, pp. 685-688.

[54] W.J. Lamb, G.A. Hoffman, and J. Jonas, “Self-diffusion in compressed supercritical water”, *Journal of Chemical Physics*, Vol. 74, 1981, pp. 6875-6880.

[55] K.H. Schmidt, P. Han, and D.M. Bartels, “Radiolytic yields of the hydrated electron from transient conductivity: Improved calculation of the hydrated electron diffusion coefficient and analysis of some diffusion-limited $(e^-)_{aq}$ reaction rates”, *Journal of Physical Chemistry*, Vol. 99, 1995, pp. 10530-10539.

[56] A.V. Bandura and S.N. Lvov, “The ionization constant of water over wide ranges of temperature and density”, *Journal of Physical and Chemical Reference Data*, Vol. 35, 2006, 15-30.

[57] J. Jortner and A. Gaathon, Effects of phase density on ionization processes and electron localization in fluids”, *Canadian Journal of Chemistry*, Vol. 55, 1977, pp. 1801-1819.

[58] H. Ohtaki, T. Radnai, and T. Yamaguchi, “Structure of water under subcritical and supercritical conditions studied by solution X-ray diffraction”, *Chemical Society Reviews*, Vol. 26, 1997, pp. 41-51.

[59] S.C. Tucker, “Solvent density inhomogeneities in supercritical fluids”, *Chemical Reviews*, Vol. 99, 1999, pp. 391-418.

[60] N. Akiya and P.E. Savage, “Roles of water for chemical reactions in high-temperature water”, *Chemical Reviews*, Vol. 102, 2002, pp. 2725-2750.

[61] J.-P. Jay-Gerin, M. Lin, Y. Katsumura, H. He, Y. Muroya, and J. Meesungnoen, “Effect of water density on the absorption maximum of hydrated electrons in sub- and supercritical water up to 400 °C”, *Journal of Chemical Physics*, Vol. 129, 2008, no. 114511.

[62] J.A. LaVerne, “Track effects of heavy ions in liquid water”, *Radiation Research*, Vol. 153, 2000, pp. 487-496.