1. Low-LET radiation chemistry of supercritical water at 400 °C:
A re-analysis of the water density dependence of the spur lifetime and the “escape” $e_\text{aq}^-$ yield

Sunuchakan Sanguanmith¹, Jintana Meesungnoen¹, David A. Guzonas²
Craig R. Stuart² and Jean-Paul Jay-Gerin¹

¹Département de Médecine Nucléaire et de Radiobiologie, Faculté de Médecine et des Sciences de la Santé, Université de Sherbrooke, 3001, 12ème Avenue Nord, Sherbrooke (Québec) J1H SN4, Canada; ²Reactor Chemistry and Corrosion Branch, Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River (Ontario) K0J 1J0, Canada

Abstract. The radiolysis of supercritical water (SCW) is an important subject for research and development of Generation-IV water-cooled nuclear reactors, which will operate at a pressure of 25 MPa and temperatures as high as ~625 °C. A key challenge in controlling the water chemistry of a SCW reactor will be mitigating the effects of water radiolysis. The formation of oxidizing products, such as $\cdot$OH, $\mathrm{H}_2\mathrm{O}_2$, $\mathrm{O}_2$, and $\mathrm{O}_2^-$ (or HO$_2^-$), by water radiolysis can significantly increase the rates of various corrosion processes and material degradation. However, the radiation-induced chemistry in SCW remains largely unknown. In addition to the very limited information on the yields of water...
radiolysis under these conditions, there are also some apparent discrepancies in existing experimental data. For example, a large difference has been noted between the hydrated electron (e\textsuperscript{−}_{aq}) yields inferred from “scavenging” experiments in irradiated low-density SCW at 400 °C from different laboratories. In this work, we first present the corrected version of a calculation that we carried out previously for the “spur lifetime” (τ\textsubscript{s}) in the γ-radiolysis of SCW (H\textsubscript{2}O) at 400 °C as a function of water density in the range of 0.15-0.6 g/cm\textsuperscript{3}. Second, using Monte Carlo simulations to model the radiolysis of SCW at 400 °C and the newly determined τ\textsubscript{s} values, we calculate the density dependence of the “escape” e\textsuperscript{−}_{aq} yield (i.e., at time τ\textsubscript{s}). Our aim is to shed more light on the apparently conflicting e\textsuperscript{−}_{aq} yield observations from different laboratories in irradiated SCW at this temperature.

**Introduction**

Generation-IV supercritical water-cooled reactors (SCWRs), which would operate at core outlet temperatures as high as ~625 °C and at a pressure of 25 MPa, are promising advanced nuclear systems because of their high thermal cycle efficiencies (~45% versus 28-32% for conventional light water reactors, thus generating lower-cost electricity). Furthermore, the simplified design of SCWRs would lead to significantly reduced capital costs.\textsuperscript{1-4}

One of the most important water chemistry challenges of SCWRs is to understand and mitigate the effects of water radiolysis. Preliminary studies suggest markedly different behavior from what is predicted from simple extrapolations of the behavior of conventional water-cooled reactors.\textsuperscript{5-7} The radiolysis of water in the supercritical regime (i.e., water above its thermodynamic critical point; for H\textsubscript{2}O: t\textsubscript{c} = 373.95 °C and p\textsubscript{c} = 22.06 MPa) and under extreme irradiation conditions (pressure of 25 MPa, temperatures as high as ~625 °C, and intense fluxes of ionizing radiation such as fast neutrons, γ-rays, recoil protons and heavy ions) leads to the formation of a variety of oxidizing products such as •OH, H\textsubscript{2}O\textsubscript{2}, O\textsubscript{2}, and O\textsubscript{2}• (or HO\textsubscript{2}•, depending on the pH). These products can significantly increase the corrosion and degradation of reactor components.\textsuperscript{5,10} However, the radiation-induced chemistry (i.e., the radiolysis yields and the rate constants of the interactions of water radiolysis products) in SCW remains largely unknown under these conditions.\textsuperscript{11,12} This paucity of data is mainly due to the fact that experiments at very high temperatures and pressures, and especially beyond the critical point of water, are difficult. In addition to the limited information on the yields of water radiolysis under supercritical conditions, there are also some apparent discrepancies in existing experimental data. For example, a large difference has been noted among “scavenging” experiments for the
hydrated electron (e\textsuperscript{−}_\text{aq}) yields\textsuperscript{1} in low-density SCW measured by Janik et al.\textsuperscript{13,14} and Haygarth and Bartels\textsuperscript{15} at the University of Notre Dame, U.S.A. (~1.5 molecules/100 eV at a density near 0.2 g/cm\textsuperscript{3}) and the values reported by Lin et al.\textsuperscript{16,17} at the University of Tokyo (~5.3 molecules/100 eV at the same density). It has been hypothesized that the N\textsubscript{2}O and SF\textsubscript{6} scavenging yield data of Bartels and co-workers and the methyl viologen (MV\textsuperscript{2+}) and 4,4′-bipyridyl scavenging results from the group of Katsumura in Tokai, Japan, may have been measured at different times.\textsuperscript{11,15,18}

The present work aims, first, to re-examine our previous calculation\textsuperscript{19} of the “spur lifetime” (τ\textsubscript{s}, defined as the time required for the changeover from non-homogeneous spur kinetics to homogeneous kinetics in the bulk solution) in the low-linear energy transfer (LET) radiolysis of SCW (H\textsubscript{2}O) at 400 °C as a function of water density in the range of ~0.15-0.6 g/cm\textsuperscript{3}. We present here a corrected version of this calculation, using a simple model of energy deposition initially in spurs, followed by diffusion of the various species of the spur until spur overlap is complete. Second, this study calculates the density dependence of the primary (or “escape”) e\textsuperscript{−}_\text{aq} yield (i.e., at time τ\textsubscript{e}) based on a stochastic model of radiolysis using Monte Carlo track chemistry calculations and the values found for τ\textsubscript{s}. By doing so, we expect to better understand the differences that have been observed experimentally in the yield of hydrated electrons in irradiated SCW at 400 °C.\textsuperscript{2}

**Spur lifetime in the low-LET radiolysis of SCW at 400 °C: Effects of water density**

To calculate the spur lifetime as a function of density at 400 °C, we used a method\textsuperscript{20,21} based primarily on the value of the LET of the studied radiation and the zigzag random (Brownian) motion of the various diffusing species formed in the radiolysis of water. Contrary to a procedure developed previously,\textsuperscript{22} based on Monte Carlo simulations of the ferrous sulfate (Fricke) dosimeter, this method is free from any effects due to the presence of oxygen or the use of scavengers. It allowed us to estimate the “mean” lifetime of a spur (τ\textsubscript{s}) by simply averaging all individual (τ\textsubscript{s}) values.

\textsuperscript{1}Throughout this paper, radiation chemical yields are quoted in units of “molecule per 100 eV”, as G\textsubscript{X} or g(X) for primary (or “escape”) yields and G(X) for experimentally measured yields. For conversion into SI units (mol/J), 1 molecule/100 eV ≈ 0.10364 μmol/J.

\textsuperscript{2}A report of this work was presented at the 6th International Symposium on Supercritical Water-Cooled Reactors, Shenzhen, Guangdong, China, March 3-7, 2013.
corresponding to each of the (main) radiolytic species \(i\) of the spur, namely, \(e^{-}_{aq}, \cdot H, \cdot OH, H_2, H_2O_2, H^+, \) and \(OH^-\). For a three-dimensional random walk, \((\tau_i)\), can be defined as\(^{23}\)

\[
r^2 = 6 D_i (\tau_i)
\]

where \(r\), the root-mean-square displacement of species \(i\) in time \((\tau_i)\), is equal to the radius of the spur (assumed to be spherical) at complete spur overlap \((i.e., \) when the spurs on expanding by diffusion will touch each other – or “percolate” – in the irradiated medium), and \(D_i\) is the diffusion coefficient of this species in the medium. As illustrated below, \(r\) can be readily calculated from the LET of the studied radiation and the average energy \((E_{av})\) being deposited in a spur:

- At 400 °C, the LET corresponding to \(~300\text{-MeV} \) incident protons (which mimic irradiation with \(^{60}\text{Co} \gamma\text{-rays or fast electrons}\) in liquid water, as obtained from our Monte Carlo track structure calculations\(^{18}\), varies as a function of water density from \(~0.048\text{ keV}/\mu\text{m} \) at 0.15 g/cm\(^3\) to \(~0.192\text{ keV}/\mu\text{m} \) at 0.6 g/cm\(^3\).
- The average energy loss per event \((i.e., \) in a spur) is \(E_{av} \sim 47\text{ eV}\).\(^{24}\)
- We want to find an integer number of interactions (spurs), which we call here \(N\), in the track segment considered. The energy required to form \(N\) spurs (assumed to be identical) is \(X = E_{av} N\). Knowing the LET \((\text{in keV}/\mu\text{m})\) of the studied radiation, we thus need a track segment of \((E_{av} N/10^3 \text{ LET}) \mu\text{m}\) for depositing \(X\) eV in it.
- Finally, the distance between two adjacent spurs in the studied track segment is \(d \) (in \(\mu\text{m}\)) = \((E_{av} N/10^3 \text{ LET})/(N - 1)\), and then \(r = d/2\). It can be seen that \(r\) depends on \(N\), the number of spurs chosen. This dependence was ignored in our previous work\(^{19}\), which led us to introduce some (relatively minor) inaccuracy in the value of \(r\). However, in light of the above calculation, this inaccuracy can be
easily corrected by choosing \( N \) as large as possible and, at the limit, infinite. Then, in this limit, the ratio \( N/(N - 1) \) becomes unity, and we have the simple result:

\[
r = \frac{E_{\text{av}}}{2 \times 10^2 \cdot \text{LET}}
\]  

(2)

where \( r \) is given in \( \mu m \) and LET in keV/\( \mu m \). For example, for a water density of 0.6 g/cm\(^3\) at 400 °C, Eq. (2) gives \( r \approx 122 \text{ nm} \). This calculation can be repeated for densities between ~0.15 and 0.6 g/cm\(^3\), knowing that the LET depends on the water density. The density dependence of \( r \), as calculated from Eq. (2), is shown in Fig. 1. As can be seen, \( r \) increases monotonically with decreasing density.

**Figure 1.** Spur radius \( r \) at complete spur overlap (i.e., at \( \tau_s \), the time required to reach homogeneity) against water density in the low-LET radiolysis of SCW at 400 °C. The solid line shows our calculated values of \( r \) from Eq. (2) in the range of 0.15-0.6 g/cm\(^3\). Note that the LET values used in Eq. (2) were obtained from our Monte Carlo track structure simulations (Ref. 18) for each density considered.
The spur lifetime for the radiolytic species \( i \) (i.e., the minimum time required before this species can be regarded as being distributed homogeneously), obtained from Eq. (1) and knowledge of \( D_i \) is \( \tau_s = r^2/6D_i \) (with \( i = e_{aq}, H^+, \cdot \text{OH}, H_2, H_2O_2, H^+, \text{and OH}^- \)).

All the radiolytic species of the spur (which are initially formed at or very near the point of energy deposition at the origin of the spur) travel (diffuse) from the origin of the sphere up to \( r \), the radius of the spur at \( \tau_s \). However, an exception is \( e_{aq} \) which is formed at \( r_o \), the “electron thermalization distance” (actually, \( r_o \) is a measure of the initial size of the spur at \( \sim 10^{-12} \) s after energy deposition). Therefore, it has to travel a distance of only \( (r - r_o) \). For the present calculation, \( r_o \) was chosen to be equal to \( \sim 3.3 \) nm and, due to a lack of more detailed information, independent of the water density.

The “average” spur lifetime \( \tau_s \) is then derived from \[ \tau_s = \frac{\sum_i (\tau_{si}) G_i}{\sum_i G_i} \] (3)

where \( G_i \) is the primary (or “escape”) yield of species \( i \) (as different radiolytic species have different primary yields, \( \tau_s \) is obtained by summing over all the individual \( (\tau_{si}) \) values corresponding to each of the species present in the spur after appropriate weightings are made according to their respective yields \( G_i \)).

The calculation above was performed for different water densities between \( \sim 0.15 \) and \( 0.6 \) g/cm\(^3\). Our calculated values of \( \tau_s \) as a function of water density are shown in Fig. 2. They are found to decrease from \( \sim 10^{-6} \) s at \( 0.15 \) g/cm\(^3\) to \( \sim 3.1 \times 10^{-8} \) s at \( 0.6 \) g/cm\(^3\). The results presented here supersede those given in our earlier paper.\(^{19}\) They reflect the fact that the distance between two adjacent spurs becomes shorter at higher density; therefore, all the species inside the spurs require a shorter time for homogeneity to become established.

“Escape” yield of \( e_{aq}^{-} \) in irradiated SCW at 400 °C: Monte Carlo computer simulations

Stochastic modeling of the low-LET radiolysis of SCW at 400 °C was performed using our Monte Carlo code IONLYS-IRT. This program simulates, in a three-dimensional space, the initial production of the various radiolytic species and the subsequent spur/track expansion, during which
these species diffuse randomly and react with one another or with dissolved solutes (if any) present at the time of irradiation. A detailed description of the code has been given previously.\textsuperscript{18,28} In brief, the IONLYS program models the early “physical” and “physicochemical” stages\textsuperscript{29} of track development. It models, on an event-by-event basis, all the physical interactions (energy deposition) and the subsequent establishment of thermal equilibrium in the system (conversion of the physical products created locally after completion of the physical stage into the various “initial” chemical species of the radiolysis). The complex spatial distribution of reactants at the end of the physicochemical stage ($\sim 10^{-12}$ s; we assume that this time also marks the beginning of diffusion), which is provided as an output of the IONLYS program, is then used directly as the starting point for the subsequent “non-homogeneous chemical” stage\textsuperscript{29} (from $\sim 10^{-12}$ s up to $\tau_s$). This third stage is modeled by our IRT program. This program employs the
“independent reaction times” (IRT) method, 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 of each pair of reactants is independent of the presence of other reactants in the system. Within the framework of this approach, the competition between the reactions is simply described via a sorting out of the stochastically sampled reaction times of each potentially reactive pair. The implementation and the validation of this program have been described in detail. Several updates were made in the present version of IONLYS-IRT. In particular, we used the radiolysis database (including rate constants, diffusion coefficients, and radiolytic yields) recently compiled by Elliot and Bartels. This new, self-consistent database provides recommendations for the best values to be used in high-temperature models of light water radiolysis up to 350 °C. Here, these data were extrapolated above their experimentally studied temperature range to obtain the rate constants of the dominant reactions involved in the radiolysis of SCW at 400 °C, as well as the diffusion coefficients of the various intervening radiolytic species). In some cases, the kinetic data of Ghandi and Percival and of Alcorn et al. inferred from muon spin spectroscopy measurements in SCW (up to 450 °C) were also used. Due to the lack of experimental data, we chose to neglect any dependence of the reaction rate constants ($k$) on water density on the 400 °C isotherm of interest. In the 0.15-0.6 g/cm$^3$ density range studied here, this approximation seems reasonable, judging from the $k$ values that vary relatively slowly for the few reactions whose rates have been measured as a function of water density. Finally, the recent re-evaluation of the temperature dependence of certain key parameters (e.g., the thermalization distance of subexcitation electrons, the dissociative electron attachment, and the branching ratios of the different excited water molecule decay channels) involved in the early physicochemical stage of radiolysis has also been incorporated in the simulations.

The density (pressure) dependence of the self-diffusion coefficient of compressed SCW at 400 °C was taken from the measurements of Lamb et al. in the region from 0.1 to 0.7 g/cm$^3$. As for the diffusion coefficients of the radiolytic species O$_2$, H$_2$O$_2$, and H$_2$, explicitly determined only at 25 °C but essentially unknown at 400 °C, we have assumed here that they scale according to the self-diffusion in water above room temperature. The diffusion coefficients of e$^-_{aq}$, H$^+$, and OH$^-$ were estimated as described previously. For the hydrated electron, we extrapolated the data of Schmidt et al. (up to 90 °C) and of Marin et al. (at 300 °C). For the proton and the
hydroxide ion, we extrapolated the data reported by Elliot and Bartels\textsuperscript{36} over the 20-350 °C temperature range. The density dependence of the viscosity, static dielectric constant, and molar concentration of SCW at 400 °C used in this work were taken from the NIST Chemistry WebBook.\textsuperscript{45} The values for the ionic product of water (K\textsubscript{w}) were obtained from Bandura and Lvov.\textsuperscript{46}

From a microscopic viewpoint, we have ignored the heterogeneous molecular structure 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 the critical point.\textsuperscript{47,48} In our simulations, we assumed that the overall instantaneous picture of SCW could simply be viewed as a continuum medium with a mean density equal to the density of bulk water. This approximation has been shown to be reasonable at the liquid-like SCW densities (around ~0.5 g/cm\textsuperscript{3}) considered in this study.\textsuperscript{18} It also seems to be justified at lower water densities considering the agreement we obtained between the model and experiments (see below).

To mimic radiolysis with \(^{60}\text{Co}\) γ-radiation or fast electrons, we used short (~100-μm) segments of ~300-MeV proton tracks, over which the LET was essentially constant and equal to ~0.3 keV/μm in normal liquid water at 25 °C. Such an analysis thus gave “track segment” yields\textsuperscript{49} as a function of time from picoseconds to, typically, microseconds. The number of proton histories (~500) was chosen so as to ensure only small statistical fluctuations when calculating average yields, while keeping acceptable computer time limits.

Figure 3 shows the calculated density dependence of the “escape” e\textsubscript{aq} yields (i.e., the yields at time \(\tau\)) for the radiolysis of pure, deaerated SCW (H\textsubscript{2}O) at 400 °C, using the newly determined spur lifetimes in Fig. 2. There is very good agreement at the highest densities (~0.4-0.6 g/cm\textsuperscript{3}) between our new computed \(g(e\textsubscript{aq})\) values and the experimental yields of e\textsubscript{aq}\textsuperscript{13-17} suggesting that the experimental data reported by the two laboratories at the University of Notre Dame and the University of Tokyo all represent the true e\textsubscript{aq} escape yields in high-density SCW. As the density decreases below ~0.4 g/cm\textsuperscript{3}, however, our calculated escape yields, although slightly larger than those reported previously,\textsuperscript{19} still compare fairly well with the experimental data of Janik et al.\textsuperscript{13,14} and Haygarth and Bartels\textsuperscript{15} (squares and circles in Fig. 3) but become much lower than those reported by Lin et al.\textsuperscript{16,17} (triangles in Fig. 3). These results suggest that the scavenged e\textsubscript{aq} yields reported by Bartels and co-workers at the University of Notre Dame (between ~0.1 and 0.4 g/cm\textsuperscript{3}) may have been measured at times that were close to the lifetimes of spurs. In that respect, the present calculations corroborate very well the recent discussion of Haygarth and Bartels\textsuperscript{15} who suggested that their “experiments probe something closer” (compared to...
Figure 3. Variation of the $e^{-}_{aq}$ yields (in molecule/100 eV) of the low-LET radiolysis of SCW at 400 °C as a function of water density over the range of ~0.15-0.6 g/cm$^3$. The dash-dot line shows our calculated primary (or “escape”) $e^{-}_{aq}$ yields assuming that $\tau_s = 60$ ns (value estimated at 400 °C)\textsuperscript{22,28,50} is constant as a function of density. The solid line represents our calculated yields using the spur lifetimes in Fig. 2. Symbols are all experimental data, shown here for comparison, obtained in SCW (H$_2$O) from different “scavenging” experiments (at 400 °C)\textsuperscript{13-17,51}.

Lin et al.’s data) to an escape yield’. In contrast, scavenging in Lin et al.’s experiments at low water density (~0.15-0.2 g/cm$^3$)\textsuperscript{16,17} could have occurred at an earlier time, probably on the order of several tens of picoseconds. This was recently suggested by Muroya et al.\textsuperscript{26,52} who first reported the kinetics of the decay of $e^{-}_{aq}$ in SCW at 400 °C, using picosecond time-resolved pulse radiolysis experiments (in H$_2$O and D$_2$O) in the range of ~60 ps to 6 ns. Interestingly, Haygarth and Bartels,\textsuperscript{15} based on scavenging power considerations, also reached a similar conclusion. In fact, these authors concluded that: “The University of Tokyo data (Lin et al.’s data\textsuperscript{16,17} shown in Fig. 3) may approach the $e^{-}_{aq}$ yields at ‘time zero’ in the spurs”.
Conclusions

In this work, we calculated the spur lifetime $\tau_s$ or, in other words, the time required for the changeover from non-homogeneous spur kinetics to homogeneous kinetics in the bulk solution in SCW at 400 °C over the density range of ~0.15-0.6 g/cm$^3$. The results show that $\tau_s$ decreases with density from $\sim 10^{-6}$ s at 0.15 g/cm$^3$ to $\sim 3.1 \times 10^{-8}$ s at 0.6 g/cm$^3$. A stochastic model of the radiolysis of SCW at 400 °C using Monte Carlo track chemistry simulations and the values found for $\tau_s$ showed that our calculated density dependence of the “escape” $e_{aq}$ yield better reproduced Bartels and co-workers’ scavenged $e_{aq}$ yield data at the lowest densities studied (below ~0.4 g/cm$^3$). This suggests that these data may have been measured at times close to $\tau_s$. This is in contrast to Lin et al.’s data which are too high to represent the “true” escape yield in low-density SCW. At the highest densities (~0.5-0.6 g/cm$^3$), however, our calculated $g(e_{aq})$ values agree quantitatively very well with both laboratories’ results.

The present calculations therefore enable us to shed more light on the apparent discrepancy that is observed among the various experimental density relationships reported so far for the $e_{aq}$ yield in irradiated SCW at 400 °C.

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