Density dependence of the spur lifetime and the "escape" hydrated electron yield in the low-LET radiolysis of supercritical water at 400 °C

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Summary

The "spur lifetime" (τ_s) in the low-LET radiolysis of supercritical water (SCW) at 400 °C has been determined as a function of density by using a simple model of energy deposition initially in spurs, followed by the random diffusion of the species formed until spur expansion is complete. The values of τ_s are found to decrease from ~5.0×10^{-6} to ~5.0×10^{-8} s over the density range ~0.15 to 0.6 g/cm^3. Using Monte-Carlo simulations, our calculated density dependence of the "escape" hydrated electron (e^-_{aq}) yield (i.e., at time τ_s) reproduces fairly well Bartels and co-workers' scavenged e^-_{aq} yield data, strongly suggesting that these data may have been measured at time close to τ_s.

1. Introduction

The radiolysis of water in the supercritical regime (t_c = 373.95 °C, p_c = 22.06 MPa and ρ_c = 0.322 g/cm^3) is an important subject in nuclear science and technology, especially for research and development of the next generation of water-cooled reactors (Gen-IV) [1]. Gen-IV supercritical water-cooled reactors (SCWRs) are promising advanced nuclear systems because of their high thermal efficiency (i.e., ~45% vs. 33% for current light water reactors) and simpler reactor designs. A key challenge in controlling the water chemistry of an SCWR will be the ability to mitigate the effects of water radiolysis [2]. The formation of oxidizing species, such as $^{\bullet}OH$, H_2O_2, O_2, and $O_2^{\bullet-}$ (or $HO_2^{\bullet}$, depending on pH), by water radiolysis can lead to corrosion and degradation of materials which can easily occur under the extreme irradiation conditions proposed for Gen-IV SCWRs (i.e., pressure of 25 MPa, temperatures as high as 625 °C, and intense flux of ionizing radiations – fast neutrons, γ-rays, recoil protons and heavy ions). However, the radiation-induced chemistry (especially, radiolytic yields and reaction rates) in SCW remains largely unknown [3]. Furthermore, there are still some apparent discrepancies on the available experimental data. For example, a strong difference has been observed in "scavenging" experiments between the e^-_{aq} yields[1] in low-density SCW measured by Bartels and co-workers [4,5] in Notre Dame, U.S.A. (1.5 molec./100 eV at a density near 0.2 g/cm^3) and those reported by Lin et al. [6,7] in Tokai, Japan (5.3 molec./100 eV at the same density). The hypothesis has been made that the N_2O and SF_6 scavenging yield data of Bartels and co-workers

[1] Throughout this paper, radiation chemical yields are quoted in units of molecules per 100 eV (abbreviated as "molec./100 eV"), as G_X or g(X) for primary (or "escape") yields and G(X) for experimentally measured yields. For conversion into SI units (mol/J): 1 molec./100 eV ≈ 0.10364 μmol/J.

and the MV^{2+} and 4,4'-bipyridyl scavenging results from Lin et al. may have been measured at different times.

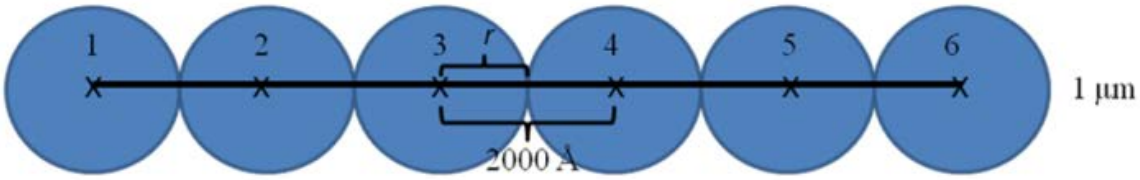
The aims of this work are two-fold; (1) to calculate the "spur lifetime" (τ_s) in the low-linear energy transfer (LET) radiolysis of SCW (H_2O) at 400 °C as a function of water density and (2) to better understand the differences that have been observed experimentally in the density dependence of the e^-_{aq} yield in irradiated SCW at 400 °C.

2. Procedure used to estimate the "spur lifetime" τ_s

To calculate τ_s as a function of density at 400 °C, we developed a simple procedure, *independent of the presence of any scavengers*, and based primarily on the value of the LET of the studied radiation and the random (Brownian) motion of the various diffusing species [8] formed in the radiolysis of water. This method allowed us to estimate a "mean" lifetime of the spur by simply averaging all individual $(\tau_s)_i$ values corresponding to each of the (main) radiolytic species, namely, e^-_{aq}, $H^\bullet$, $^\bullet H$, H_2, H_2O_2, H^+, and OH^-. For a 3D random walk, $(\tau_s)_i$ can be defined as [9]

$$r^2 = 6 D_i (\tau_s)_i \quad (1)$$

where r is 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) and D_i is the diffusion coefficient of the species i in the medium. As illustrated below, r can be calculated from the LET of the considered radiation and the average energy being deposited in a spur.



- For ~300-MeV incident protons in liquid water at 25 °C (mimicking an irradiation with ^{60}Co γ-rays or fast electrons): LET ~ 0.3 keV/µm.
- Average energy loss in a spur: ~47 eV (as obtained from our Monte-Carlo track-structure calculations [10]), that is, 6 interactions (or "spurs") in a ~1-µm proton track length.
- Distance between two adjacent spurs: 1 µm/5 ≈ 2000 Å → r ≈ 2000 Å/2 = 1000 Å.
- Spur lifetime for the species i (minimum time required before this species can be regarded as being homogeneously distributed), inferred from Eq. (1): $(\tau_s)_i = r^2/6 D_i$ (i = e^-_{aq}, $H^\bullet$, $^\bullet OH$, H_2, H_2O_2, H^+, OH^-).
- "Average" spur lifetime: $\tau_s = \dfrac{\sum_i (\tau_s)_i G_i}{\sum_i G_i}$

where G_i is the primary (or "escape") yield of the species i [11] (as different radiolytic species

have different primary yields, the "average" spur lifetime is obtained by summing over all the individual $(\tau_s)_i$ values corresponding to each of the species present in the spur after appropriate weighting is made according to their respective yields G_i).

This calculation was repeated here at 400 °C at different densities between ~0.15 and 0.6 g/cm^3.

3. Monte-Carlo simulations

The stochastic modeling of the low-LET radiolysis of SCW (H_2O) at 400 °C was performed using our Monte-Carlo code IONLYS-IRT that simulates, in a 3D geometrical environment, the initial production of the various radiolytic species and the subsequent diffusion and chemical reactions of these species. The detailed description of the code is given in ref. [12]. This code has, however, been updated here using the radiolysis database (including rate constants, reaction mechanisms, and *G*-values) recently compiled by Elliot and Bartels [13]. The re-evaluation of certain parameters (e.g., the thermalization distance of subexcitation electrons) that intervene in the early physicochemical stage of the radiolysis has also been incorporated [14].

4. Results and discussion

Our calculated values of τ_s as a function of water density at 400 °C are shown in Fig. 1. They are found to decrease from ~5.0 × 10^{-6} s at 0.15 g/cm^3 to ~5.0 × 10^{-8} s at 0.6 g/cm^3. Such a result

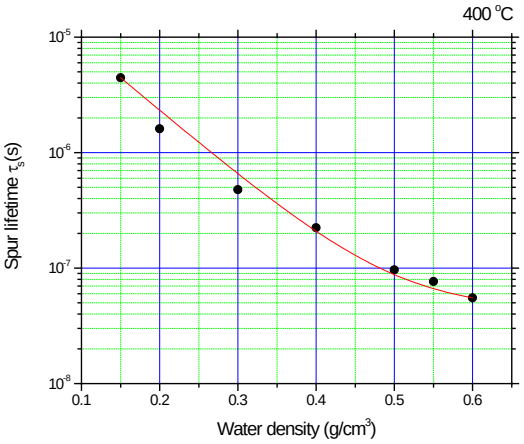


Figure 1 Spur lifetime vs. water density in the low-LET radiolysis of SCW at 400 °C. The solid circles show our calculated values of τ_s, the red line being there only to guide the eye.

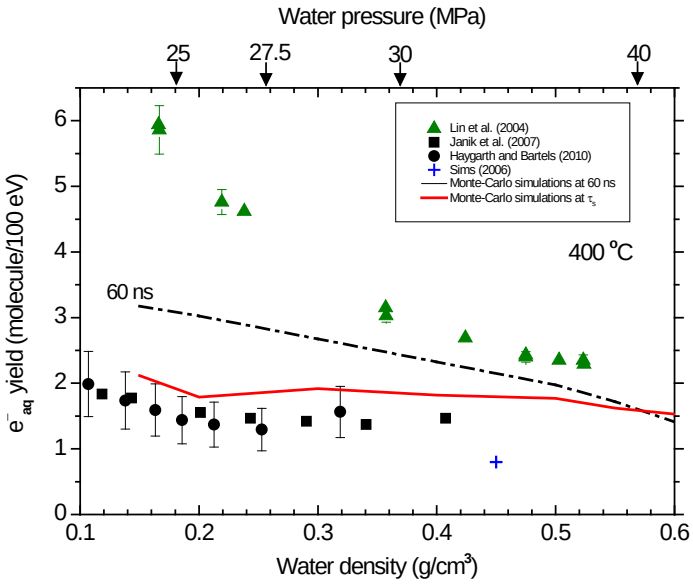


Figure 2 e^-_{aq} yield (in molec./100 eV) vs. water density in the low-LET radiolysis of SCW (H_2O) at 400 °C. The dash-dot line shows our calculated primary (or "escape") e^-_{aq} yields assuming that τ_s = 60 ns is constant as a function of the density [15,16]. The solid (red) line shows our calculated yields using the spur lifetimes shown in Fig. 1. Symbols are experimental data [4-7,17] shown for comparison.

reflects the fact that the distance between two adjacent spurs becomes shorter at higher density, and therefore all the species inside the spurs will require a *shorter* time for homogeneity to become established.

As we can see from Fig. 2, our calculated density dependence of the "escape" e^-_{aq} yields (that is, the yields at times τ_s) – using the spur expansion times shown in Fig. 1 – reproduces fairly well the experimental data of Bartels and co-workers [4,5]. These results suggest strongly that the scavenged e^-_{aq} yields reported by these authors may have been measured at times that are close to the lifetimes of the spurs. In that respect, the present calculations corroborate very well the recent discussion of Haygarth and Bartels [5] who suggested that their "*experiments probe something close to an escape yield*". In contrast, scavenging in Lin et al.'s experiments [6,7] could have occurred at earlier time, of the order of a few nanoseconds at high water density (~0.5-0.6 g/cm^3) but probably of the order of several tens of picoseconds at low water density (~0.15-0.2 g/cm^3) as recently suggested by Muroya et al. [18] who first reported the kinetics of the decay of e^-_{aq} in SCW (D_2O) at 400 °C, using picosecond time-resolved pulse radiolysis experiments in the range ~60 ps to 6 ns.

5. Conclusion

In this work, we calculated the spur lifetime τ_s or, in other words, the time required for the changeover from nonhomogeneous spur kinetics to homogeneous kinetics in the bulk solution in SCW at 400 °C over the density range ~0.15 to 0.6 g/cm^3. The results show that τ_s decreases with density from ~5.0 × 10^{-6} s at 0.15 g/cm^3 to ~5.0 × 10^{-8} s at 0.6 g/cm^3. The stochastic modeling of the radiolysis of SCW at 400 °C using Monte-Carlo simulations and the values thus found for τ_s showed that our calculated density dependence of the "escape" e^-_{aq} yield reproduced fairly well Bartels and co-workers' scavenged e^-_{aq} yield data, suggesting strongly that these data may have been measured at times close to τ_s. The present results thus shed new light on the apparent discrepancy that is observed in the various experimental density dependences reported so far for the e^-_{aq} yield in irradiated SCW at 400 °C.

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6. References

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