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DENSITY DEPENDENCE OF THE RADIOLYSIS YIELDS OF PRIMARY SPECIES FROM FAST NEUTRON-IRRADIATED SUPERCRITICAL WATER AT 400 °C

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Abstract

A reliable understanding of radiolysis processes in supercritical water (SCW)-cooled reactors is crucial to developing chemistry control strategies that minimize corrosion and the transport of both corrosion products and radionuclides. Chemistry control is one of the most important factors to keep the integrity of materials from degradation processes and also to reduce out-of-core radiation fields and worker dose. However, directly measuring the chemistry in reactor cores is difficult due to the extreme conditions of high temperature and pressure and mixed neutron and γ-radiation fields that are not compatible with normal chemical instrumentation. Thus, chemical models and computer simulations are an important route of investigation for predicting the detailed radiation chemistry of the coolant in a SCW reactor and the consequences for materials. Surprisingly, there is only limited information on the fast neutron radiolysis of water at high temperatures, and no experimental data are yet available on the radiolysis yields for fast neutron irradiation of SCW. In this work, Monte Carlo simulations were used to predict the *G*-values for the primary species e^-_{aq}, $H^\bullet$, H_2, $^\bullet OH$, and H_2O_2 formed from the radiolysis of pure, deaerated SCW (H_2O) by 2-MeV mono-energetic neutrons at 400 °C as a function of water density in the range of ~0.15-0.6 g/cm^3. The 2-MeV neutron was taken as representative of a fast neutron flux in a reactor. For light water, the moderation of these neutrons after knock-on collisions with water molecules generated mostly recoil protons of 1.264, 0.465, 0.171, and 0.063 MeV having linear energy transfer (LET) values of ~3.3, 6.5, 10.4, and 11.4 keV/μm at 0.15 g/cm^3, and ~13.3, 26, 42, and 46 keV/μm at 0.6 g/cm^3, respectively. Neglecting oxygen ion recoils and assuming that the most significant contribution to the radiolysis came from these first four recoil protons, the fast neutron yields were estimated as the sum of the *G*-values for these protons after appropriate weightings were applied according to their energy. Calculated yields were compared with available experimental data and with data obtained for low-LET (^{60}Co γ-rays or fast electrons) radiation. Most interestingly, the reaction of $H^\bullet$ atoms with water was found to play a critical role in the formation yields of H_2 and $^\bullet OH$ at 400 °C. Recent work has recognized the potential importance of this reaction above 200 °C, but its rate constant is still controversial.

Keywords: Generation IV supercritical water (SCW) reactor, radiolysis, high temperature, fast neutrons, recoil protons, γ-irradiation, linear energy transfer (LET), scavenging capacity, primary species, radiolytic yields (*G*-values), Monte Carlo track chemistry simulations.

1. Introduction

The "Generation IV" supercritical water-cooled reactor (SCWR) is being considered as a future advanced nuclear reactor system whose main advantages are based on significant savings in capital costs due to plant simplification, increased thermodynamic efficiency realized by heating the water to higher temperatures (greater than ~45% versus ~33% for current in-service light water reactors), and enhanced passive safety characteristics [1,2]. However, one of the most significant water chemistry challenges for any SCWR design is to understand and mitigate the effects of water radiolysis; the reactors under consideration [3-10] would operate with core inlet and outlet temperatures of ~350 to 625 °C, respectively, and at a pressure of 25 MPa. The action of mixed neutron/γ-radiation fields on water under such extreme conditions (*i.e.*, water in the supercritical regime, well above its thermodynamic critical point; for H_2O: $t_c = 373.95$ °C, $P_c = 22.06$ MPa, and $\rho_c = 0.322$ g/cm^3; for D_2O: $t_c = 370.74$ °C, $P_c = 21.67$ MPa, and $\rho_c = 0.358$ g/cm^3 [11]) results in the radiolytic formation of oxidizing species, such as $^{\bullet}OH$, H_2O_2, O_2, and $O_2^{\bullet-}$ (or $HO_2^{\bullet}$, depending on the pH). These products are highly reactive with most metal alloys and can significantly increase the corrosion and degradation of reactor components [8,12-14].

A reliable understanding of the radiation chemistry of the coolant water in a SCWR environment is required to specify a chemical control strategy that will minimize the degradation of materials. Currently employed in CANDU pressurized heavy water reactors is the addition of a small amount of excess H_2 to the reactor coolant to chemically limit the net radiolytic production of oxidizing species. It is still unclear, however, whether this mitigation strategy would also be effective under SCW conditions. When describing radiolysis and water chemistry in reactors, there are two key parameters that need to be determined: 1) the chemical yields (reported as *G*-values, or numbers of species formed or destroyed per 100 eV of absorbed energy) of species from both low-LET γ- and high-LET fast-neutron-radiolysis, and 2) the rate constants for all of the chemical reactions involving these species and any other chemicals present in the system. However, the chemistry induced in water by neutrons remains largely unknown for the proposed SCWR operating conditions [7,8,10,15]. As far as we know, there is only one experimental study in the literature on the determination of radiolytic yields for fast neutron irradiation of SCW, namely, that of Eric Edwards [10] reported in his doctoral thesis at the University of Wisconsin-Madison in 2007.

Direct measurements of the chemistry in and around the reactor core region are difficult due to the extreme conditions of high temperature, pressure, and mixed (fast neutrons/γ-rays) radiation fields. Moreover, Generation IV SCWRs are currently at the stage of conceptual designs. For these reasons, chemical models and computer simulations are an important route of investigation for predicting the detailed radiation chemistry of water in a SCW reactor and the consequences for materials.

In this work, Monte Carlo calculations were undertaken to predict the *G*-values for the primary species e^-_{aq}, $H^•$, H_2, $^•OH$, and H_2O_2 resulting from the radiolysis of pure, deaerated SCW (H_2O) by incident mono-energetic 2-MeV neutrons at 400 °C as a function of water density in the range of ~0.15 to 0.6 g/cm^3. The 2-MeV energy of neutrons was taken as representative of the average initial energy of a fast fission neutron flux in a reactor [16-19].

2. Fast neutron interaction with water

The interaction of the neutron depends strongly on its kinetic energy. For "fast" neutrons (*i.e.*, those with kinetic energies ranging from ~0.5 to 10 MeV) that concern us in this work, most of the slowing down occurs through a process of many successive "billiard-ball" elastic collisions with atomic nuclei, following the simple laws of conservation of energy and momentum of classical particle physics [20]. In elastic scattering, the total kinetic energy of the neutron and nucleus is unchanged by the interaction. During the interaction, a fraction of the neutron's kinetic energy is transferred to the nucleus. In the case of the fast neutron radiolysis of water and aqueous solutions, the neutrons are "moderated" by both hydrogen (proton) and oxygen nuclei. Thereby, a spectrum of recoil-ion energies is produced from which the LET along the track of each released recoil charged particle can be assigned and the chemical yields for the various species formed can be obtained.

The proton and oxygen ion recoils generated by the passage of the incident neutron are widely separated from one another along the path of the neutron [21]. Moreover, these recoil nuclei – whose energy is distributed from zero to the energy of the incident neutrons – have maximum "ranges" (*i.e.*, track lengths) much less than the average separation between two successive neutron interactions. The mean free path of a 2-MeV neutron in water is about 4 cm, while the recoil proton and oxygen ion maximum ranges for this energy are ~75.5 and 1.5 μm, respectively [21]. Thus, these elastically scattered protons and oxygen ions can be considered as behaving *independently* of each other: their ionizing energy is deposited locally in dense tracks in the water in the immediate vicinity of the collision sites (the points of generation of the recoil particles) with virtually no allowance for overlap of the reaction zones of neighboring tracks. As a consequence, under normal irradiation conditions, the observed water radiolysis chemistry should tend to resemble that induced by independent, high-LET protons and oxygen ions losing their energy in dense tracks.

For light water, it can be shown [17,21-23] that the most significant contribution to the radiolysis comes from the *first four neutron collisions* that, in the case of a 2-MeV neutron, generate recoil protons having energies of 1.264, 0.465, 0.171, and 0.063 MeV [24]. Lower energy protons are ignored since they do not contribute significantly to the radiolysis. Neglecting the radiation effects due to oxygen ion recoils [25], the fast neutron yields could be estimated on the basis of the *G*-values for these four recoil protons only.

The energy of a recoil proton can be calculated using the equation [17,21,26]

$$\ln\left(\frac{E_0}{E_n}\right) = n\left[1 + \frac{(A-1)^2}{2A}\ln\left(\frac{A-1}{A+1}\right)\right], \qquad (1)$$

where A is the mass number of the struck nucleus (A = 1 for collisions with protons [27]), E_0 is the initial neutron kinetic energy, and E_n is the average energy of the neutron after n individual elastic scattering collisions. The quantity $E_{p1} = (E_0 - E_1)$ is the energy imparted to the first recoil proton, and so on.

For a 2-MeV neutron, the final neutron yields were then calculated by summing the G-values for each of the above four recoil protons (obtained from our Monte Carlo simulations) weighted by its fraction of the total neutron energy absorbed [17,21-23]:

$$G(\mathrm{X}) = \frac{\sum_{\mathrm{i}=1}^{4}\left(G(\mathrm{X})_{p_\mathrm{i}}\, E_{p_\mathrm{i}}\right)}{E_\mathrm{T}}, \qquad (2)$$

where $G(\mathrm{X})_{p_\mathrm{i}}$ is the free radical or molecular yield associated with the recoil proton p_i (i = 1 to 4) and

$$E_\mathrm{T} = \sum_{\mathrm{i}=1}^{4} E_{p_\mathrm{i}} \qquad (3)$$

is the sum of all recoil proton energies.

3. Monte Carlo simulations

The sequence of events that are generated in the fast neutron radiolysis of SCW by impacting protons of various initial energies was modelled using an extended version [28,29] of our Monte Carlo simulation code called IONLYS-IRT [30]. Briefly, the IONLYS step-by-step simulation program is used to cover the early *physical* and *physicochemical* stages of radiation action up to ~10^{-12} s in the track development. The species created on this time scale rapidly reorganize and produce the “initial” free radicals and molecular products e^-_{aq}, H^+, OH^-, $H^\bullet$, H_2, $^\bullet OH$, H_2O_2, $O_2^{\bullet-}$ (or $HO_2^\bullet$, depending on pH), $^\bullet O^\bullet$, etc., of the radiolysis. The complex, highly nonhomogeneous spatial distribution of reactants 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. This third stage, during which the individual radiolytic species diffuse randomly and react with each other (or with the environment) until all track processes are complete, is covered by our IRT program. This program employs the *independent reaction times* (IRT) method [31,32], a computer-efficient stochastic simulation technique that is used to simulate reaction times without following the trajectories of the diffusing species. Its implementation has been described in detail previously [33] and its ability to give accurate, time-dependent chemical yields has been well validated by comparison with full random flights (or “step-by-step”) Monte Carlo simulations, which do follow the reactant trajectories in detail [34,35]. This IRT program can also be used to efficiently describe the reactions that occur in the bulk solution during the *homogeneous chemical* stage, *i.e.*, in the time domain beyond typically a few microseconds.

In the current version of IONLYS-IRT, several updates and modifications have been made, as fully described in [29,36,37]. In particular, we used the self-consistent radiolysis database (including rate constants, diffusion coefficients, and radiolytic yields) recently compiled by Elliot and Bartels [19] (over the range of 20-350 °C). These data were simply extrapolated above their experimentally studied temperature range to obtain the rate constants of the various reactions involved in the radiolysis of SCW at 400 °C, as well as the diffusion coefficients of the intervening reactive species. In some cases, the kinetic data of Ghandi and Percival [38] and of Alcorn *et al.* [39] inferred from muon spin spectroscopy measurements in subcritical water and 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 for the 400 °C isotherm of interest. In the 0.15-0.6 g/cm^3 density range studied here, this approximation does not seem to have a large impact, judging from the relatively slowly varying k values for the few reactions whose rates have been measured as a function of water density [9,39-42]. The recent re-evaluation of the temperature dependence of certain key parameters involved in the early physicochemical stage of radiolysis (*i.e.*, the electron thermalization distance, the dissociative electron attachment, and the branching ratios of the different excited water molecule decay channels) has also been incorporated in the simulations [36,37]. Finally, we included in the simulations a prompt geminate electron-cation ($H_2O^{\bullet+}$) recombination (*i.e.*, prior to the thermalization of the electron) that decreased in irradiated SCW at 400 °C as the water density decreased from ~0.6 to 0.15 g/cm^3 [29].

The density (pressure) dependence of the self-diffusion coefficient of compressed SCW at 400 °C was taken from the measurements of Lamb *et al.* [43] in the region from 0.1 to 0.7 g/cm^3. As for the diffusion coefficients of the radiolytic species $^\bullet OH$, $H^\bullet$, H_2O_2, and H_2, explicitly determined only at 25 °C and essentially unknown at 400 °C, we assumed here that they scale proportionally to the self-diffusion of water above room temperature [28,43,44]. The diffusion coefficients of e^-_{aq}, H^+, and OH^- were estimated as described previously [28]. For the hydrated electron, we extrapolated the data of Schmidt *et al.* [45] (up to 90 °C) and of Marin *et al.* [46] (at 300 °C). For the proton and the hydroxide ion, we extrapolated the data reported by Elliot and Bartels [19] over the 20-350 °C temperature range. The density dependences of the viscosity, static dielectric constant, and molar concentration of SCW at 400 °C used in this study were taken from the NIST Chemistry WebBook [11]. The values for the ionic product of water (K_w) were obtained from Bandura and Lvov [47].

From a microscopic viewpoint, we ignored the heterogeneous molecular structure of SCW originating from the existence of large local density fluctuations (or water “clustering”) that are fundamentally connected to the high compressibility of water in the vicinity of the critical point [48,49]. In our simulations, we assumed that the overall instantaneous picture of SCW could simply be viewed as a *homogeneous* medium with a *mean* density equal to the density of bulk water. This approximation has been shown to be reasonable in SCW at 400 °C at the water densities considered in this study [28,50].

To reproduce the effects due to 2-MeV neutrons, we simulated short (~15-150 μm) track segments of each of the first four generated recoil protons. Over these simulated track segments, the energy and LET of the protons were well defined and remained nearly constant. Such model calculations thus gave track segment yields at a well-defined LET. The number of proton histories (usually ~10-150, depending on the proton energy, but up to ~500 at low water densities) was chosen so as to ensure only small statistical fluctuations in the computed averages of chemical yields, while keeping acceptable computer time limits. The total neutron yields of the various radiolytic products were then calculated by summing the corresponding weighted *G*-values for each recoil proton according to Eq. (2).

4. Results and discussion

Our computed yields of e^-_{aq}, $H^\bullet$, H_2, $^\bullet OH$, and H_2O_2 in pure, deaerated supercritical water (H_2O) irradiated by 2-MeV incident neutrons at 400 °C are shown in Fig. 1 as a function of water density in the range of 0.15-0.6 g/cm^3. Our *G*-values were calculated at three different times, namely 10^{-7}, 10^{-6}, and 10^{-5} s after the ionization event (solid, dashed, and dotted red lines in Fig. 1, respectively), here chosen in accordance with the time scales associated with the “scavenging powers” [18,51] of solutes (in the range of ~10^5-10^7 s^{-1}) generally used in scavenging experiments to measure the yields.

To our knowledge, the only experimental work that reports measurements of neutron radiolysis yields at SCW conditions is that by Edwards [10] using an apparatus designed for this purpose [15] at the University of Wisconsin Nuclear Reactor. Neutron *G*-values for e^-_{aq}, $H^\bullet$, and H_2 were measured at high temperatures from 25 to 430 °C at a constant pressure of ~25 MPa, and at both 380 and 400 °C as a function of water density (in the range of ~0.17-0.53 g/cm^3 and ~0.12-0.41 g/cm^3, respectively), using various chemical scavenging systems. Unfortunately, at 400 °C, yields for $H^\bullet$ and H_2 were found by the author [10] to be well beyond realistic levels, suggesting the intervention of a radiation catalyzed chain reaction that creates an excess signal not indicative of true *G*-values). As a result, these data could not be used here to compare with our calculated $G(H^\bullet)$ and $G(H_2)$ values. In contrast, the aqueous electron yield results, inferred from sulfur hexafluoride (SF_6) scavenging experiments in SCW-phenol solutions at neutral pH, were considered accurate by the author [10]. However, as shown in Fig. 1(a), the density dependence of these SF_6 scavenging yields could not be satisfactorily reproduced by our computed $G(e^-_{aq})$ values.

In fact, using the SF_6 concentration (2.8×10^{-4} *M*) employed in Edwards’ experiments [10] and the value of ~2×10^{11} M^{-1} s^{-1} for the ($e^-_{aq} + SF_6$) reaction rate constant measured by Cline *et al.* [42] at 380 °C (nearly constant for the density range studied), we obtain a scavenging time [51] of electrons by SF_6 of ~2×10^{-8} s. In Fig. 1(a), it can be seen that this time is roughly three orders of magnitude shorter than what one would expect at low water densities around ~0.15 g/cm^3 [$G(e^-_{aq})$ ~ 0.5 molecule/100 eV at ~10^{-5} s] from our simulations [see also Fig. 2(a)]. Moreover, examination of the density dependence of Edwards’ e^-_{aq} yields indicates that $G(e^-_{aq})$, which reaches ~1.25 molecules/100 eV at the highest density studied by the author (~0.41 g/cm^3), could be extrapolated to values of ~2 to 3 molecules/100 eV in the liquid-like density

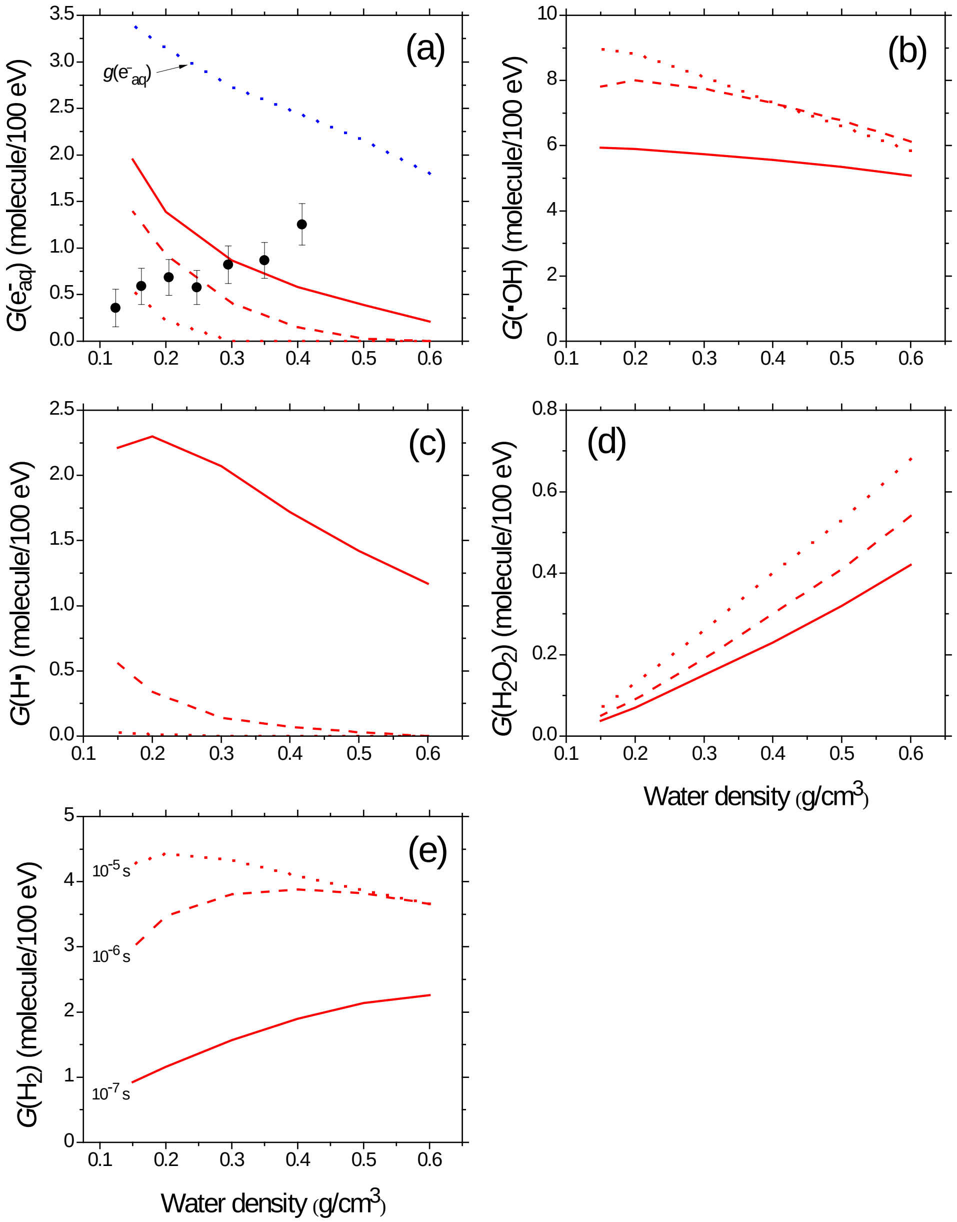

Figure 1: Variation of the G-values (in molecule/100 eV) for the radiolysis of pure, deaerated SCW (H_2O) by 2-MeV neutrons at 400 °C as a function of water density in the range of 0.15-0.6 g/cm^3: (a) $G(e^-_{aq})$, (b) $G(^{\bullet}OH)$, (c) $G(^{\bullet}H)$, (d) $G(H_2O_2)$, and (e) $G(H_2)$. Our simulated results, obtained at 10^{-7}, 10^{-6}, and 10^{-5} s based on the radiation effects in 1.264, 0.465, 0.171, and 0.063 MeV recoil proton tracks, are shown as solid, dashed, and dotted red lines, respectively. Experimental data for $G(e^-_{aq})$ (●) obtained using sulfur hexafluoride (SF_6) as scavenger for e^-_{aq} in SCW-phenol solutions at neutral pH [10]. For the sake of comparison, the blue dotted line shows our calculated density dependence of the *primary* (or "escape") e^-_{aq} yield, denoted by $g(e^-_{aq})$, for the low-LET radiolysis of SCW at 400 °C using our previously calculated *spur lifetime* (τ_s) values [29,50,52]. Throughout this paper, radiation chemical yields are given in the units of "molecule per 100 eV"; for conversion into SI units (mol/J), 1 molecule/100 eV ≈ 0.10364 μmol/J.

region near 0.6 g/cm^3. Such values are *not* consistent with experimental neutron radiolysis yields of e^-_{aq} reported in the literature between 25 and 350 °C [53]. Indeed, extrapolation of existing data shows that $G(e^-_{aq})$ could hardly be higher than ~0.5-0.75 molecule/100 eV at 400 °C [53]. In light of these above considerations, we are inclined to think that Edwards' *G*-values for e^-_{aq}, just as for $H^•$ and H_2, are questionable or erroneous, and that further measurements would be highly desirable. At present, they cannot be used with confidence to compare with our results.

Compared with the *primary* e^-_{aq} yield data obtained for low-LET (γ-rays from ^{60}Co or fast electrons) SCW radiolysis at 400 °C [29,50,52], our computed fast neutron radiolysis yield $G(e^-_{aq})$ shows an essentially similar density dependence over the range of density studied, but with (much) *lower* values [see Fig. 1(a)]. This result directly reflects the *high-LET character of fast neutrons* [18,19,53]. Indeed, upon increasing the LET of the radiation, an increased intervention of radical-radical reactions is taking place as the local concentration of radicals along the radiation track is high and many radical interactions occur before the products can escape into the bulk solution. This allows more radicals to undergo combination and recombination reactions during the expansion of the tracks and in turn leads to a decreased proportion of radical products (in favor of the molecular products) [30].

The effect of density (pressure) on the various yields shown in Fig. 1 can be understood as follows. As we lower the density in SCW, there are fewer water molecules to present a physical "barrier" or, in other words, a solvent "cage effect" [54]. This results in the *increased cage escape of free radicals* originating from water dissociation [40,42], as the proximity condition that would allow them to combine or recombine and lead to molecular products is not favored. In contrast, these density effects act in the opposite direction in the high-density liquid-like region, where a large barrier of solvent is present. In this case, the caged free radical products are forced to remain as colliding neighbors within the ion track where they are formed and recombine, thereby *increasing the molecular yields*. This is in agreement with what we observe in Fig. 1 (see also Fig. 2).

To illustrate this point, Fig. 2 shows the time evolutions of $G(e^-_{aq})$ and $G(^•OH)$ calculated from our Monte Carlo simulations of the radiolysis of SCW at 400 °C by 2-MeV neutrons at two fixed densities, 0.15 and 0.6 g/cm^3. Inspection of the time dependence of the cumulative e^-_{aq} yield variations for the different reactions (see Table 1) that contribute to $G(e^-_{aq})$ (data not shown here) indicates that the decay of $G(e^-_{aq})$ is mostly due to the fast charge-recombination reaction R1 of e^-_{aq} with H^+ (~71%) and to the reaction R2 of e^-_{aq} with $^•OH$ (~22%). In comparison, the other reactions, such as R3, R4, and R5, are relatively unimportant (~7%). Interestingly, these results closely parallel those obtained for the radiolysis of SCW at 400 °C by low-LET radiation [28,36,55]. As for the $^•OH$ radical, the main oxidizing radical species formed in this 2-MeV fast neutron radiolysis, the temporal dependence of its decay is found to be dominated by reaction R2, rather than by reactions R9 or R7. If reaction R4 contributes virtually nothing in the formation of $^•OH$, our calculations show a marked increase of $G(^•OH)$ at times longer than ~10^{-8}-10^{-7} s (depending on the density) resulting from the oxidation of water by the $H^•$ atom (reaction R6) in the homogeneous chemical stage.

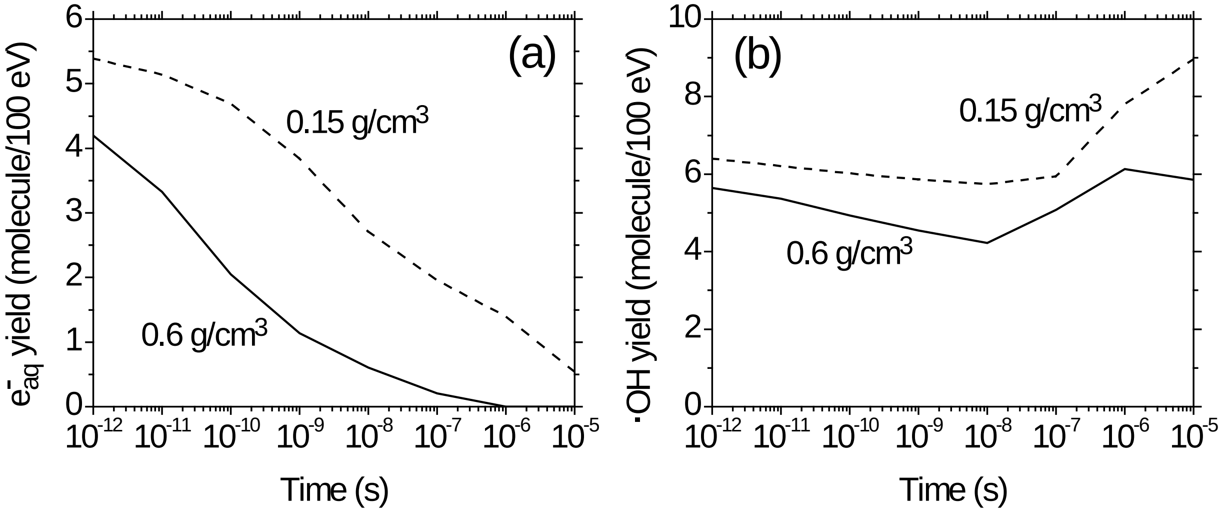

Figure 2: Variation of the yields of e^-_{aq} (a) and $^{\bullet}OH$ (b) (in molecule/100 eV) computed from our Monte Carlo simulations of the radiolysis of pure, deaerated SCW (H_2O) by 2-MeV incident neutrons as a function of time from 10^{-12} to 10^{-5} s, for the two fixed water densities: 0.15 and 0.6 g/cm^3 (dashed and solid lines, respectively) at 400 °C.

It is interesting to recall here that reaction R6 was proposed to quantitatively explain the large, anomalous increase of the primary yield of H_2 observed experimentally in the low-LET radiolysis of water at elevated temperatures [19,37,56-59]. Recent work has recognized the potential importance of this reaction above 200 °C, but a controversy currently exists regarding its rate constant. Notwithstanding the recent experimental estimate of Ghandi and co-workers [39] using muonium as an analogue of the hydrogen atom (1.1×10^4 M^{-1} s^{-1} at 300 °C, with an error of ~38%), the values for the latter reported thus far in the literature span a range of more than one order of magnitude (from 1.5×10^3 to 3.2×10^4 M^{-1} s^{-1} at ~300 °C) and remain largely uncertain. As a result of this uncertainty, no clear conclusion has yet been obtained as to the real contribution of reaction R6 in radiolysis as a possible source, at high temperatures and even more so in SCW, of $^{\bullet}OH$ radicals and molecular hydrogen.

5. Conclusion

In this work, Monte Carlo simulations were used to calculate the *G*-values for the primary species of the radiolysis of pure, deaerated SCW (H_2O) by mono-energetic 2-MeV neutrons at 400 °C as a function of water density in the range of 0.15-0.6 g/cm^3. The fast neutron *G*-values were obtained by assuming that the most significant contribution to the radiolysis comes from the first four elastically scattered recoil protons generated by the passage of the incident neutron and by neglecting the radiation effects due to oxygen ion recoils. Our computed e^-_{aq} yield values were found to disagree with the only available experimental data in the literature. However, based on various considerations, we were led to the conclusion that these measured *G*-values for e^-_{aq} were questionable and could not be used with confidence for comparison with our results. Compared with the data obtained for low-LET radiation, our calculated e^-_{aq} yields

Reaction	Symbol	k (M^{-1} s^{-1})
R1	$e^-_{aq} + H^+ \rightarrow H^\bullet$	3×10^{12}
R2	$e^-_{aq} + {}^\bullet OH \rightarrow OH^-$	4.5×10^{11}
R3	$e^-_{aq} + H^\bullet\ (+ H_2O) \rightarrow H_2 + OH^-$	3.5×10^{11}
R4	$e^-_{aq} + H_2O_2 \rightarrow {}^\bullet OH + OH^-$	4.7×10^{11}
R5	$e^-_{aq} + e^-_{aq}\ (+ 2\ H_2O) \rightarrow H_2 + 2\ OH^-$	4.2×10^{8}
R6	$H^\bullet + H_2O \rightarrow {}^\bullet OH + H_2$	2.2×10^{5}
R7	$H^\bullet + {}^\bullet OH \rightarrow H_2O$	4.4×10^{10}
R8	$H^\bullet + H^\bullet \rightarrow H_2$	1.5×10^{11}
R9	${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2$	8.5×10^{9}
R10	$H^+ + HO_2^- \rightarrow H_2O_2$	1.2×10^{12}

Table 1: Main chemical reactions and their corresponding rate constants (k) at 400 °C used in our IRT simulations. Note that, in the calculations, it was assumed that the temperature dependence of the rate constant for reaction R6 could be described by an Arrhenius relationship, based on an estimate of ~4.6 $\times 10^{-5}$ M^{-1} s^{-1} at 25 °C [19] and 10^4 M^{-1} s^{-1} at 300 °C [39], then extrapolated to obtain the rate constant at 400 °C. Moreover, in the absence of any other information, we simply assumed that all reaction rate constants remained constant with water density on the 400 °C isotherm of interest.

for fast neutrons showed an essentially similar density dependence over the range of densities studied, but with lower values: a result reflecting the high-LET character of fast neutrons. Finally, a striking feature of our simulated results obtained at 400 °C was the marked increase, at long times, of $G(H_2)$ and $G({}^\bullet OH)$ and the corresponding decrease of $G(H^\bullet)$, due to the occurrence of the reaction $H^\bullet + H_2O \rightarrow H_2 + {}^\bullet OH$ in the homogeneous chemical stage. This reaction is a source of H_2 formation, which is an important component associated with the corrosion environment of the coolant system in nuclear power plants. Knowledge of the production of H_2 from water radiolysis and the optimum H_2 concentration (the so-called "critical hydrogen concentration") needed to add into the primary coolant to mitigate water decomposition (if this strategy applies under SCWR conditions) is indeed crucial for chemistry control and to optimize plant performance.

More experimental data are required to better describe the dependence of radiolytic yields on density, to test more thoroughly our modeling calculations, and to specify the potential role of the reaction of hydrogen atoms with water at high temperatures.

6. Acknowledgement

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