

## LOW-LINEAR ENERGY TRANSFER RADIOLYSIS OF SUPERCRITICAL WATER AT 400 °C: DENSITY DEPENDENCE OF THE G( $\cdot$ OH)

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### ABSTRACT

**LOW-LINEAR ENERGY TRANSFER RADIOLYSIS OF SUPERCRITICAL WATER AT 400 °C: DENSITY DEPENDENCE OF THE G( $\cdot$ OH).** Monte Carlo simulations were used to predict the yield of primary specie  $\cdot$ OH denoted as  $g(\cdot\text{OH})$  that is formed from the radiolysis of pure, deaerated supercritical water (SCW) ( $\text{H}_2\text{O}$ ) at 400 °C in the range of water density between  $\sim 0.15$  and  $0.6 \text{ g/cm}^3$ . It is known that  $\cdot$ OH, is one of the oxidizing species that significantly can increase the possibility of various corrosion and material degradation as well. The thorough radiolysis processes in SCW-cooled reactor is not established currently, and it is believed to be a challenge in developing chemistry control strategies for future Supercritical Water Reactor (SCWR). Since SCWR technology is now still under the conceptual design, hence there is only limited information published on the yields of radiolysis under these conditions. In this work,  $g(\cdot\text{OH})$  was calculated at spur lifetime ( $\tau_s$ / minimum time needed before the species within spur distributed homogeneously into the bulk solution),  $10^{-7}$  and  $10^{-6}$  sec after the ionization event at all densities. From this work, it is shown that the data measured by other researcher at lower density ( $< 0.35 \text{ g/cm}^3$ ) is taken at longer time, while at higher density ( $> 0.35 \text{ g/cm}^3$ ) is taken about near the spur lifetime. Finally, more experimental data are highly required in order to examine more thoroughly modeling calculation.

**Keywords:** low-LET radiation radiolysis, yields (g-value), Monte Carlo, SCWR, water density

### ABSTRAK

**RADIOLISIS LOW-LINEAR ENERGY TRANSFER PADA AIR SUPER KRITIS PADA TEMPERATUR 400 °C: PENGARUH DENSITAS PADA G( $\cdot$ OH).** Simulasi Monte Carlo digunakan untuk memprediksi yield pada spesies primer  $\cdot$ OH yang dilambangkan sebagai  $g(\cdot\text{OH})$  yang terbentuk dari radiolisis air superkritis (SCW) setelah teraerasi pada temperatur 400 °C dengan rentang densitas antara  $\sim 0.15$  and  $0.6 \text{ g/cm}^3$ . Diketahui bahwa  $\cdot$ OH, adalah salah satu spesies pengoksidasi yang secara signifikan dapat meningkatkan kemungkinan berbagai jenis korosi dan degradasi material. Proses radiolisis pada reactor berpendingin SCW (SCWR) belum banyak tersedia di literatur; dan akan menjadi suatu tantangan dalam mengembangkan strategi pengendalian kimia air SCWR. Oleh karena teknologi SCWR masih dalam tahapan desain konseptual, dengan demikian informasi nilai yields untuk produk radiolisis pada kondisi ini sangat terbatas. Pada penelitian ini,  $g(\cdot\text{OH})$  dihitung pada spur lifetime ( $\tau_s$ / waktu minimum yang dibutuhkan sebelum spesies yang ada di dalam spur terdistribusi secara homogen di dalam larutan),  $10^{-7}$  dan  $10^{-6}$  detik setelah ionisasi terjadi pada semua rentang densitas. Dari penelitian ini, disimpulkan bahwa data yang diperoleh oleh peneliti lainnya pada densitas rendah ( $< 0.35 \text{ g/cm}^3$ ) diperoleh pada waktu yang lebih lama, sementara pada densitas yang lebih tinggi ( $> 0.35 \text{ g/cm}^3$ ) diperoleh pada waktu spur lifetime. Oleh karena itu, ketersediaan data eksperimen sangat diharapkan untuk menguji keseluruhan perhitungan model ini.

**Kata kunci:** radiolisis Low-LET radiation, yields (g-value), Monte Carlo, SCWR, densitas air

## INTRODUCTION

Supercritical water-cooled reactor (SCWR) is considered as one of the future promising nuclear reactors among the six reactor technologies that are studied intensively. It is due to the plant simplicity and its high thermal efficiency could reach greater than ~45% (compared with ~33% for current in-service light water reactors (LWRs)), thus produces lower-cost electricity, which meets the goals that have been set for Generation IV nuclear energy systems [1,2]. SCWR is a high temperature, high pressure super critical water-cooled reactor that is considered to be operated at ~300 to 625 °C, at a pressure of 25 MPa (above the thermodynamic critical point of water 374 °C and 22.1 MPa) and under mixed neutron/ $\gamma$ -radiation fields. Reactor coolant experiences single phase condition during its circulation throughout the reactor core. However, the proper water chemistry in using super critical water (SCW) remains largely unclear. One of the challenge in applying the water chemistry strategy is the issue of water radiolysis that can generate degradation of reactor primary component such as in LWR [3,4]. It is interesting to investigate the water radiolysis under such this condition, due to the increase of temperature as well as the changes in water properties and water structure, which would strongly affect the reactions occurred in the spur (an area formed by the ionizing radiation after the deposition of its energy on the matter). Hence, some interesting changes of the radiolytic yielding under supercritical conditions are expected. In this work,

the density variation in the range of 0.15 – 0.6 g/cm<sup>3</sup> is represented.

Since SCWR is still under conceptual design, this is being said that, a radiolysis well-controlled experiment of super critical water is very difficult to perform especially beyond the critical point of water, thus the available data (in this case, concentration of oxidizing species) are very limited. While waiting for the experimental data to be available, we considered that it is necessary to model the sequences of all radiolysis process to predict the concentration of redox species, which are the product of radiation induced SCW decomposition. In this case, Monte Carlo, developed by J.-P. Jay-Gerin group in the Universite de Sherbrooke, Quebec, Canada, is an important part of investigation for predicting the detailed radiation chemistry of the cooling water in a SCW reactor and the consequences for materials. In order to investigate the radiolysis product, there are two important key parameters needed, which are: (1) the knowledge of temperature dependent reaction rate constant of all the involved species and (2) the chemical yields or *g*-values (denoting the number of species formed or destroyed per 100 eV of absorbed energy) of the species for  $\gamma$ -rays (low Linear Energy Transfer / LET) and fast neutrons (high LET). It is expected that the changes of these properties would reflect on *g*-values.

The radiolysis products, in particular oxidizing species (in this case  $\cdot\text{OH}$ ), contribute to induce corrosion, hydriding, and crac-

king in reactor components material <sup>[5]</sup>. In other words, concentration of this radical is a dominant factor of corrosive environment. In this work, we attempt to investigate the density dependence of  $g(\cdot\text{OH})$  and compare the results with the most recent experimental results obtained in the studies of radiation chemistry on SCW using Monte Carlo simulations.

There are few measured  $g$ -values at SCW and have large uncertainties, and also they are often published in the sum of several species, not the individual value, therefore it is very difficult to extract. To the best of our knowledge, the only work that have been done in determining the  $\cdot\text{OH}$ , is namely the work of Lin et al <sup>[6]</sup> using scavenger method. Then our calculated  $g(\cdot\text{OH})$  was compared to their work and also to the works that have been reported for radiolysis of pure, deaerated SCW by incident monoenergetic 2-MeV neutrons and  $\beta$ -particle at 400 °C as a function of water density.

## METHODOLOGY

Monte Carlo code IONLYS-IRT was carried out to model the complexity interaction between low-LET radiations with SCW <sup>[7]</sup>. IONLYS *step-by-step* code performs all the events that take place at very early time, which are *physical* ( $<10^{-15}$  s) and *physico-chemical* ( $\sim 10^{-15}$  -  $10^{-12}$  s) stages during the track development. The species formed at this time scale are the “initial” free radicals and molecular products of the radiolysis i.e.  $e^-_{\text{aq}}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{H}^\cdot$ ,  $\text{H}_2$ ,  $\cdot\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2^{\cdot\ominus}$  (or  $\text{HO}_2^\cdot$ , depending on pH),  $\cdot\text{O}$ , etc. These species being said as the output of the IONLYS pro-

gram, were then used right away as the starting point for *nonhomogeneous chemical* stage (at the time scale from  $\sim 10^{-12}$  s up to  $\sim 10^{-7}$ - $10^{-6}$  s at 25 °C). This third stage was performed by IRT program <sup>[8,9]</sup>, where the previously-mentioned-radiolytic species diffuse and react with one another until all track processes are complete. The *independent reaction times* (IRT) method is a computer-efficient stochastic simulation technique, that is used to simulate reaction times without having to follow the trajectories of the diffusing species. Its ability to provide accurate time-dependent chemical yields has been well validated by comparison with full random flights (or *step-by-step*) Monte Carlo simulations that follow the reactant trajectories in detail <sup>[10]</sup>.

In the current version of IONLYS-IRT several updates and modifications regarding SCW condition have been made as described in several researches <sup>[7, 11, 12]</sup>. The list of chemical reactions between radiolytic products, values of reaction rate constants, and diffusion coefficients were taken from recently report compiled by Elliot and Bartels <sup>[13]</sup>. The author recommended the best values that can be used to model water radiolysis over the range of 20 - 350 °C. Due to the lack of experimental data for SCW regime, in this work, to obtain the rate constants of the dominant reactions involved in the radiolysis of SCW at 400 °C, we simply extrapolated above their experimentally studied temperature range, which is possible, as well as the diffusion coefficients of the various intervening radiolytic species. The kinetic data of Ghandi and Percival <sup>[14]</sup> and of

Alcorn et al. [15] inferred from muon spin spectroscopy measurements in SCW (up to 450 °C) were also used. In addition, the dependence of the reaction rate constants ( $k$ ) on water density on the 400 °C was neglected, since this value varies relatively slowly for the few reactions [16]. Also we have been incorporated an early time geminate electron-cation ( $\text{H}_2\text{O}^{\bullet+}$ ) recombination (prior thermalization of the electron) effect that decreased as the density decreased [17].

The density (pressure) dependence of the self-diffusion coefficient of SCW at 400 °C has been taken into account in the region from 0.1 to 0.7 g/cm<sup>3</sup>. For the diffusion coefficients of the radiolytic species  $\bullet\text{OH}$ ,  $\text{H}\bullet$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2$ , we have estimated them by scaling proportionally to the self-diffusion of water above the room temperature [18]. The diffusion coefficients of  $e_{\text{aq}}^-$ ,  $\text{H}^+$ , and  $\text{OH}^-$  were estimated as described in ref. [18]. 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, while the values for the ionic product of water ( $K_w$ ) were obtained from Bandura and Lvov [19]. In this present work, 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.

To mimic radiolysis with <sup>60</sup>Co  $\gamma$ -radiation or fast electrons, we simulated short ( $\sim 100$   $\mu\text{m}$ ) segments of  $\sim 300$  MeV proton tracks, over which the LET was essentially constant and

equal to  $\sim 0.3$  keV/ $\mu\text{m}$  in normal liquid water at 25 °C. The number of proton histories (usually  $\sim 500$ ) was chosen so as to ensure only small statistical fluctuations in the computed averages of chemical yields, while keeping acceptable computer time limits.

## RESULTS AND DISCUSSION

The  $g$ -values for the primary specie  $\bullet\text{OH}$  formed from the radiolysis of pure, deaerated SCW ( $\text{H}_2\text{O}$ ) by low LET gamma radiolysis at 400 °C have been calculated as a function of water density in the range of  $\sim 0.15$ - $0.6$  g/cm<sup>3</sup> and have been compared with available experimental data and other modeled or estimated  $g$ -values results as shown in Fig. 1. This results are important in reaching the long goal, to predict the concentrations of oxidizing species, in this case  $\bullet\text{OH}$ , that contribute in causing the corrosion of material structure in the reactor core under the SCWR conditions. Thus, the studies of the reaction of  $\bullet\text{OH}$  radical at supercritical water are essential.

Our  $g$ -values were calculated at  $\tau_s$  (minimum time needed before the species within spur distributed homogeneously into the bulk solution),  $10^{-7}$  and  $10^{-6}$  s after the ionization event at all densities (solid and dashed lines in Fig. 1, respectively), as a function of density in the low-LET radiolysis of SCW as reported by Sanguanmith et al [20]. They calculated the density dependence of spur lifetime using the Brownian motion of the various diffused species. Their work showed that  $\tau_s$  decrease from  $\sim 10^{-6}$  s at 0.15 g/cm<sup>3</sup> to  $\sim 3.1 \times 10^{-8}$  s at 0.6 g/cm<sup>3</sup>. There is a reasonable good

agreement between our calculated  $g(\cdot\text{OH})$  value and the experimental yield reported by Lin et al that is measured using 100 mM  $\text{NaHCO}_3$  or a deaerated solution of 100 mM  $\text{NaHCO}_3$  in the presence of 1 mM  $\text{NaNO}_3$  as scavenger of  $\cdot\text{OH}$ . There is a similar density dependence of  $g(\cdot\text{OH})$  between our calculated data at  $\tau_s$  and Lin's data, which is decreasing monotonically as density increases. From this work, it is shown that the data measured by Lin et.al, at low density ( $<0.35 \text{ g/cm}^3$ ) is taken at longer time, while at higher density ( $>0.35 \text{ g/cm}^3$ ) was taken about near the spur lifetime. Our results proposed that yield  $\cdot\text{OH}$  was measured at longer time and the reverse phenomenon occurred at higher density. In addition to that our computed data at  $\tau_s$  show essentially similar density dependences over the range of density studied with 2 MeV fast neutron [21], but with *lower* values. This general trend is due to the *high-LET character of fast neutrons*.

The decreasing of the free radical  $g(\cdot\text{OH})$  as a function of density can be readily explain due to the distance of two adjacent spurs, which are shorter as the density increases, thereby, the probability to react with other species are higher, or in other words the 'escape' yields becomes lower. The decay of  $\cdot\text{OH}$  could take faster at higher density as can be seen in Fig. 2, or in other words the recombination between two radicals are more favorable, due to the distance between two spurs adjacent as explained earlier.

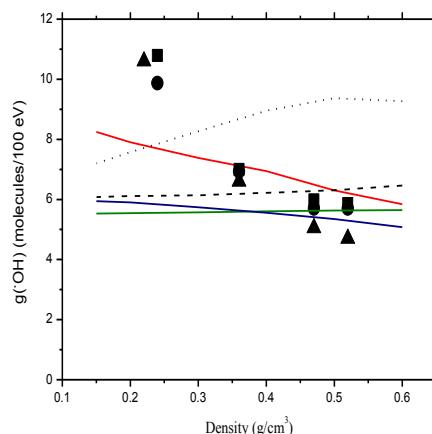


Fig. 1. Density dependence of the  $g(\cdot\text{OH})$  (in molecule/100 eV) for the SCW radiolysis in the range of  $\sim 0.15\text{-}0.6 \text{ g/cm}^3$

Figure 1 shows our calculated results obtained at  $\tau_s$ ,  $10^{-7}$  and  $10^{-6}$  s. (red solid line, black dashed and black dotted lines). Experimental data are from: [18] ( $\bullet$ ,  $\blacktriangle$ ,  $\blacksquare$ ) (using  $\text{NaHCO}_3$ ). The blue solid line shows the 2 MeV fast neutron calculated  $g$ -values [21]. The olive solid lines are the results for  $\beta$ -particle [22]. The red solid line shows the estimated primary (or "escape") yields for the low-LET ( $\sim 0.3 \text{ keV}/\mu\text{m}$ ) radiolysis of water [20].

Figure 2 shows the time dependence of  $g(\cdot\text{OH})$  (from  $10^{-12}$  to  $10^{-6}$  s at two fixed density of  $0.15$ , dashed line, and  $0.6 \text{ g/cm}^3$ , solid line), it can be seen clearly that its decay took faster at higher density, as exposed, and there is a curvature at longer time for density  $0.6 \text{ g/cm}^3$  corresponding to the reaction no. 1 (R-1):  $\text{H}^{\cdot} + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}_2$ . For  $\cdot\text{OH}$ , as the main

oxidizing radical formed by water radiolysis, the main reactions (in order of decreasing importance, the data not shown here) that contribute to form this radical are the oxidation of water by  $H^\bullet$ , reaction (R1) and the reaction no. 2 (R-2):  $e_{aq}^- + H_2O_2 \rightarrow \cdot OH + OH^-$  of  $e_{aq}^-$  and  $H_2O_2$  over the density studied.

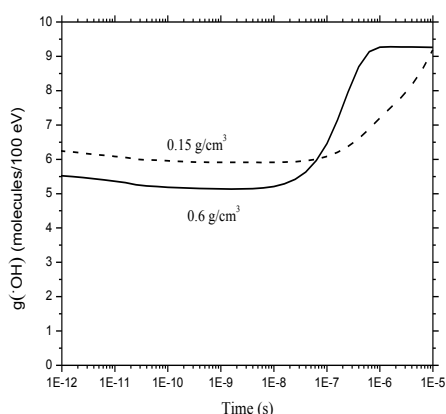


Fig. 2. Time evolution of the yields of  $\cdot OH$  (in molecule/100 eV) computed from Monte Carlo simulations

It seems that our earlier assumption about the distance between two adjacent spurs is correct, considering that  $H_2O_2$  was not forming significantly yet at lower density since the reaction of two radicals are not favored significantly. The decay of hydroxyl radical is dominated by reaction no. 3 (R-3):  $e_{aq}^- + \cdot OH \rightarrow OH^-$  rather than its recombination of reaction 4 (R-4):  $\cdot OH + \cdot OH \rightarrow H_2O_2$ . It is interesting to highlight here that reaction (R1) was found to play a critical role as one of the important reaction in the formation yields of  $H_2$  and  $\cdot OH$ , and correspondence in the consumption of  $H^\bullet$  at 400 °C, as also concluded in our previous work [21,22]. Recent work has recognized the potential im-

portance of this reaction above 200 °C, that has been reported elsewhere. Regarding this reaction, no clear conclusion has yet been obtained as to the real contribution of this potentially important reaction in the radiolysis of water as a function of temperatures and pressure (density).

## CONCLUSION

In this work, we calculated the  $g(\cdot OH)$  of the pure SCW at 400 °C as a function of pure water in the range of  $\sim 0.15$ - $0.6$   $g/cm^3$  using Monte Carlo simulation. The  $g(\cdot OH)$  is calculated at three different times which is at  $\tau_s$ ,  $10^{-7}$  and  $10^{-6}$  s. There is a reasonable good agreement between our calculated  $g(\cdot OH)$  value and the experimental yield reported by Lin et al. The similar density dependence of  $g(\cdot OH)$  between our calculated data at  $\tau_s$  and Lin's data is obviously seen, which decreases monotonically as density increases. The present calculations enable us to explain the discrepancy that is observed among the experimental and calculated data for the hydroxyl radical yield in irradiated SCW at 400 °C.

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