

## Article

# A Numerical Simulation of Radiation Chemistry for Controlling the Oxidising Environment in Water-Cooled Nuclear Power Reactors

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**Abstract:** Maintaining the integrity of materials of light-water nuclear power reactors requires the development of effective methods to control and minimise the corrosive environment associated with the radiolysis of a coolant. In this study, the behaviour of the oxidising environment is simulated using a hybrid method. The hybrid method has advantages in that the production of radiolytic species under exposure of the coolant to ionising radiation is simulated while providing material and charge balances. Steady-state concentrations of stable and transient oxidising agents are calculated as a function of radiation composition and dose rate by numerical integration of the system of kinetic equations describing radiation chemistry of neutral water, the alkaline solution, and the hydrogenated systems at 300 °C. The importance of the reactions and equilibria constituting the radiolysis scheme of the coolant is assessed. The influence of the presence of a base and the injected H<sub>2</sub> on the yield of key reactions responsible for the formation of the main oxidants H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> are discussed. Simulation indicated the synergic effect of H<sub>2</sub> gas and base added to the coolant on diminishment of the steady-state concentration of oxidants.



**Citation:** Swiatla-Wojcik, D. A Numerical Simulation of Radiation Chemistry for Controlling the Oxidising Environment in Water-Cooled Nuclear Power Reactors. *Appl. Sci.* **2022**, *12*, 947. <https://doi.org/10.3390/app12030947>

Academic Editor: Maria Filomena Botelho

Received: 20 December 2021

Accepted: 14 January 2022

Published: 18 January 2022

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**Keywords:** LWR coolant chemistry; chemical kinetics; high-temperature water radiolysis; nuclear power engineering; numerical simulation; sensitivity analysis

## 1. Introduction

Light-water reactors (LWRs), categorised into boiling-water reactors (BWRs) and pressurised-water reactors (PWRs), are the most widespread type of nuclear power reactors [1]. In LWRs, water plays a role of a neutron moderator and a coolant. The cooling water operates at high pressure and temperature conditions (7–7.5 MPa, 285 °C in BWRs and ca. 15.5 MPa, 315 °C in PWRs) and is exposed to intense fluxes of gamma rays and fast neutrons [2] (pp. 960–1023). Exposition to ionising radiation results in the formation of transient radical species: hydrated electrons ( $e_{aq}^{\bullet-}$ ), hydroxyl radicals ( $\cdot OH$ ), hydrogen radical atoms ( $H\cdot$ ), hydroperoxyl radicals ( $HO_2\cdot$ ), ions:  $H_3O^+$ ,  $OH^-$ ,  $O_2^-$ ,  $HO_2^-$ ,  $O^-$ , and stable molecular products: molecular hydrogen (H<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), molecular oxygen (O<sub>2</sub>) [3] (pp. 331–364). The stable oxidants (H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>) create a corrosive environment contributing significantly to stress corrosion cracking of the structural materials [1,2,4–6]. The harmful effect of oxidants is strengthened by the low acidity (low pH) of water at the operating temperatures. For example, because the ionic product of water ( $K_w$ ) abruptly increases with temperature, the pH of liquid neutral water is 5.8 at 300 °C, compared with pH 7 at 25 °C. To minimise the concentration of dissolved oxidants and increase pH, the chemicals such as H<sub>2</sub>, hydrazine (N<sub>2</sub>H<sub>4</sub>), ammonia (NH<sub>3</sub>), lithium hydroxide (LiOH) are added to the coolant [1]. A quantitative understanding of how these additives change a corrosive environment in the nuclear core is still insufficient but essential to control stress corrosion cracking and maintain the integrity of materials in reactor circuits. In particular, it is important to estimate critical hydrogen concentration

(CHC), i.e., the amount of dissolved hydrogen gas needed to suppress the net production of  $O_2$  and  $H_2O_2$  in the reactor circuit [2] (pp. 960–1023).

Direct measurements of the chemical environment at the reactor core are not feasible because of high pressure, high temperature, and intense radiation field. Analysis of the reactor water is possible only at sampling points far away from circulation lines. Therefore, computer simulation is indispensable to model the radiation chemistry of the coolant under different operational conditions and assess the response of the oxidising environment to the additives ( $H_2$ ,  $LiOH$ ,  $N_2H_4$ ,  $NH_3$ ).

As knowledge of high-temperature water radiolysis develops the simulations have been widely applied to estimate the chemistry of the coolant, both in the core and in associated pipelines [7–14]. Usually, simulation of the coolant chemistry is based on the numerical solution of a set of ordinary differential equations describing reactions of the primary and secondary chemical species, which are formed during the exposition of cooling water to ionising radiation. The reliability of such a simulation largely depends on the accuracy of the input data including rate constants for the zero-, first-, and second-order reactions. The former rate constants are directly related to the radiation chemical yields of the primary species formed in ca.  $10^{-7}$  s after the ionising event [3] and expressed in the number of species per 100 eV of energy deposited in the medium.

During the past few decades, the input data for the simulation of the high-temperature radiolysis of water have been amassed by several research groups based on the measurements or extrapolation of the data available for lower temperatures [13,15,16]. The variations between outputs of simulations using the datasets from different laboratories were examined by Katsumura et al. [13]. These authors found variations particularly resulting from uncertainties in the primary yields of  $\cdot OH$ ,  $H_2$ , and  $H_2O_2$  for neutron radiolysis, and confirmed the significance of reaction (42) between  $H\cdot$  and  $H_2O$  (Table 1) indicated by the earlier simulations of the coolant chemistry [8,10]. Later simulation using the hybrid method showed that the uncertainty in the rate constant of  $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  may result in the unsureness of the estimated steady-state concentration of  $H_2$ ,  $H_2O_2$ , and  $O_2$  of 17, 9, and 4  $\mu\text{M}$ , respectively [14].

**Table 1.** Production rates  $P_{i(g)}$  and  $P_{i(n)}$  of the primary species obtained assuming the dose rate value of  $1 \text{ kGy} \cdot \text{s}^{-1}$  and using the G values for gamma and fast neutron radiolysis of water at  $300^\circ \text{C}$  from ref. [14]. Last row describes loss of water molecules resulting from irradiation.

| Species <i>i</i>    | $P_{i(g)}, \text{M} \cdot \text{s}^{-1}$ | $P_{i(n)}, \text{M} \cdot \text{s}^{-1}$ |
|---------------------|------------------------------------------|------------------------------------------|
| $e_{aq}^{\bullet-}$ | $2.385 \cdot 10^{-4}$                    | $1.062 \cdot 10^{-4}$                    |
| $H\cdot$            | $5.970 \cdot 10^{-5}$                    | $5.455 \cdot 10^{-05}$                   |
| $H^+$               | $2.837 \cdot 10^{-4}$                    | $1.453 \cdot 10^{-4}$                    |
| $\cdot OH$          | $3.564 \cdot 10^{-4}$                    | $2.730 \cdot 10^{-4}$                    |
| $H_2O_2$            | $1.866 \cdot 10^{-5}$                    | $3.201 \cdot 10^{-5}$                    |
| $H_2$               | $4.776 \cdot 10^{-5}$                    | $8.895 \cdot 10^{-5}$                    |
| $HO_2\cdot$         | 0                                        | $5.584 \cdot 10^{-7}$                    |
| $OH^-$              | $4.522 \cdot 10^{-5}$                    | $3.910 \cdot 10^{-5}$                    |
| $-H_2O$             | $3.937 \cdot 10^{-4}$                    | $3.387 \cdot 10^{-4}$                    |

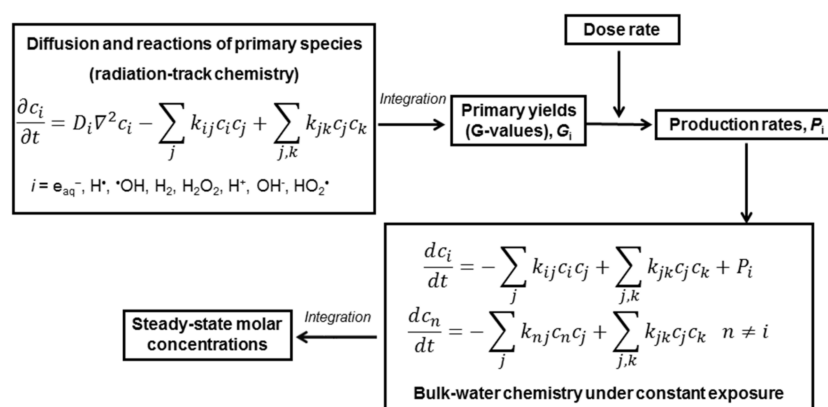
Since 2005, the role of reaction (42) in the radiolysis of water at high temperatures has been under intensive scientific debate [17–22]. One of the difficulties in recognising the importance of water oxidation by  $H\cdot$  in the liquid phase results from high activation energy [19] and a negligibly slow rate at ambient conditions [18,19,23]. The latest pulse radiolysis measurements in an aqueous iodide solution showed an increase in the rate constants, from ca.  $4 \times 10^3$  to  $6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , in a temperature range of  $270$ – $350^\circ \text{C}$  [22]. These measurements confirmed earlier evaluations using thermodynamics [19] and muonium chemistry [21].

In this study, we exploited the hybrid method for numerical simulation of LWR coolant chemistry [14] and the measured high-temperature rate of water oxidation by

H<sup>•</sup> [22] to identify the principal reactions responsible for the production of oxidants in the pressurised liquid water exposed to gamma ( $\gamma$ ) and fast neutron radiation at 300 °C. Steady-state concentrations of oxidants calculated assuming averaged values of reaction rate constants reported from different laboratories are presented for mixed radiation as a function of gamma to fast neutron dose rate ratio ranging from 0 to 1. The effectiveness of additives such as H<sub>2</sub> and LiOH in suppressing the production of stable oxidants is simulated and discussed.

## 2. Materials and Methods

Numerical simulations were performed using the hybrid method, described in detail elsewhere [14] and schematically illustrated in Scheme 1. The concept of the hybrid method is to combine diffusion–kinetic calculation for the radiolytic species initially clustered in radiation tracks and kinetic calculation of reactants homogeneously distributed in the bulk solvent. Numerical integration of a set of diffusion–kinetic equations up to 0.1  $\mu$ s provided the primary yields (or G values) of the primary species ( $e_{aq}^{•-}$ ,  $^{\bullet}OH$ ,  $H^{\bullet}$ ,  $H^+$ ,  $OH^-$ ,  $H_2$ ,  $H_2O_2$ ,  $HO_2^{\bullet}$ ). The primary yields, still often expressed in molecules per 100 eV of absorbed energy, were then recalculated to production rates  $P_i$  according to the required dose rate. Simulations were performed for the dose rates of 1 and 10  $kGy \cdot s^{-1}$ , which are similar to the in-core dose rates of gamma and fast neutron radiation.



**Scheme 1.** Schematic illustration of the hybrid method [14]:  $c_i$  and  $D_i$  are molar concentrations and diffusion coefficients of the primary species;  $P_i$  (in  $M \cdot s^{-1}$ ) =  $1.0364 \cdot 10^{-7} \cdot G_i$  (in molecules per 100 eV)  $\cdot$  (dose rate in  $Gy \cdot s^{-1}$ )  $\cdot$  (water density in  $kg \cdot dm^{-3}$ ) is a production rate of the  $i$ -th primary species under constant exposure to ionising radiation.

Table 1 presents production rates  $P_{i(g)}$  and  $P_{i(n)}$ , obtained for gamma and fast neutron radiolysis of water at 300 °C. For mixed radiation, production rates were calculated using the equation  $P_{i(mix)} = f_g P_{i(g)} + f_n P_{i(n)}$ , where  $f_g + f_n = 1$ .

The advantage of employing the hybrid method is that the production of primary radiolytic species satisfies both the material balance and the charge balance. At the concentration of additives  $[OH^-] = 2 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$  and  $[H_2] \leq 1.5 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ , considered in this study, the production rates for alkaline and hydrogenated solutions can be assumed the same as for neutral water at 300 °C [24].

The production rates specified in Table 1 were used as zeroth-order terms in a system of differential kinetic equations, which was defined with respect to 13 species (i.e.,  $e_{aq}^{•-}$ ,  $^{\bullet}OH$ ,  $H^{\bullet}$ ,  $OH^-$ ,  $H_2O$ ,  $H_2$ ,  $H_2O_2$ ,  $O_2$ ,  $O_2^{•-}$ ,  $HO_2^{\bullet}$ ,  $HO_2^-$ ,  $H_2$ ,  $H_2O_2$ ,  $O^{\bullet-}$ ,  $O_3^{•-}$ ,  $O^{\bullet}$ ) involved in the 1st and 2nd order reactions listed in Table 2. The reaction set and the associated high-temperature rate constants were compiled based on the data reported from different laboratories.

**Table 2.** Reaction set for the radiolysis of high-temperature water and rate constants  $k$  at 300 °C (units for 2nd and 1st order reactions are  $M^{-1} \cdot s^{-1}$  and  $s^{-1}$ , respectively). For reactions between similar species, the value of  $k$ , not  $2k$ , is given.

| No.             | Reaction                                                                 | $k$ (300 °C)         | No.             | Reaction                                                                                           | $k$ (300 °C)         |
|-----------------|--------------------------------------------------------------------------|----------------------|-----------------|----------------------------------------------------------------------------------------------------|----------------------|
| 1 <sup>1</sup>  | $e_{aq}^{\bullet-} + e_{aq}^{\bullet-} \xrightarrow{+2H_2O} H_2 + 2OH^-$ | $6.06 \cdot 10^6$    | 30 <sup>1</sup> | $H^+ + HO_2^- \rightarrow H_2O_2$                                                                  | $5.69 \cdot 10^{11}$ |
| 2 <sup>2</sup>  | $H^{\bullet} + H^{\bullet} \rightarrow H_2$                              | $1.01 \cdot 10^{11}$ | 31 <sup>1</sup> | $H_2O_2 \rightarrow H^+ + HO_2^-$                                                                  | $2.52 \cdot 10^1$    |
| 3 <sup>2</sup>  | $\bullet OH + \bullet OH \rightarrow H_2O_2$                             | $1.80 \cdot 10^{10}$ | 32 <sup>1</sup> | $H^+ + O^{\bullet-} \rightarrow \bullet OH$                                                        | $5.69 \cdot 10^{11}$ |
| 4 <sup>2</sup>  | $e_{aq}^{\bullet-} + H^{\bullet} \xrightarrow{+H_2O} H_2 + OH^-$         | $4.39 \cdot 10^{11}$ | 33 <sup>1</sup> | $\bullet OH \rightarrow H^+ + O^{\bullet-}$                                                        | $2.52 \cdot 10^1$    |
| 5 <sup>2</sup>  | $e_{aq}^{\bullet-} + \bullet OH \rightarrow OH^-$                        | $4.69 \cdot 10^{11}$ | 34 <sup>1</sup> | $H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$                                                          | $1.36 \cdot 10^{11}$ |
| 6 <sup>2</sup>  | $H^{\bullet} + \bullet OH \rightarrow H_2O$                              | $5.52 \cdot 10^{10}$ | 35 <sup>1</sup> | $HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$                                                          | $1.76 \cdot 10^8$    |
| 7 <sup>2</sup>  | $e_{aq}^{\bullet-} + H_2O_2 \rightarrow OH^- + \bullet OH$               | $2.73 \cdot 10^{11}$ | 36 <sup>1</sup> | $HO_2^{\bullet} + OH^- \rightarrow O_2^{\bullet-} + H_2O$                                          | $2.87 \cdot 10^4$    |
| 8 <sup>2</sup>  | $e_{aq}^{\bullet-} + O_2 \rightarrow O_2^{\bullet-}$                     | $2.49 \cdot 10^{11}$ | 37 <sup>1</sup> | $O_2^{\bullet-} + H_2O \rightarrow HO_2^{\bullet} + OH^-$                                          | $1.36 \cdot 10^{11}$ |
| 9 <sup>1</sup>  | $e_{aq}^{\bullet-} + O_2^{\bullet-} \xrightarrow{+2H_2O} H_2O_2 + 2OH^-$ | $1.61 \cdot 10^{11}$ | 38 <sup>1</sup> | $H^+ + e_{aq}^{\bullet-} \rightarrow H^{\bullet}$                                                  | $7.16 \cdot 10^{11}$ |
| 10 <sup>3</sup> | $e_{aq}^{\bullet-} + O_2^{\bullet-} \xrightarrow{+H_2O} HO_2^- + OH^-$   | $2.15 \cdot 10^{11}$ | 39 <sup>1</sup> | $H^{\bullet} \rightarrow H^+ + e_{aq}^{\bullet-}$                                                  | $1.65 \cdot 10^5$    |
| 11 <sup>2</sup> | $e_{aq}^{\bullet-} + HO_2^{\bullet} \rightarrow HO_2^-$                  | $2.46 \cdot 10^{11}$ | 40 <sup>2</sup> | $H^{\bullet} + OH^- \rightarrow e_{aq}^{\bullet-} + H_2O$                                          | $2.26 \cdot 10^{10}$ |
| 12 <sup>2</sup> | $H^{\bullet} + H_2O_2 \rightarrow \bullet OH + H_2O$                     | $1.29 \cdot 10^9$    | 41 <sup>2</sup> | $e_{aq}^{\bullet-} + H_2O \rightarrow H^{\bullet} + OH^-$                                          | $1.16 \cdot 10^3$    |
| 13 <sup>2</sup> | $H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$                           | $1.11 \cdot 10^{11}$ | 42 <sup>4</sup> | $H^{\bullet} + H_2O \rightarrow \bullet OH + H_2$                                                  | $3.04 \cdot 10^4$    |
| 14 <sup>3</sup> | $H^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2$                        | $3.31 \cdot 10^{11}$ | 43 <sup>2</sup> | $\bullet OH + H_2 \rightarrow H^{\bullet} + H_2O$                                                  | $1.15 \cdot 10^9$    |
| 15 <sup>1</sup> | $H^{\bullet} + HO_2^{\bullet} \rightarrow 2\bullet OH$                   | $2.14 \cdot 10^{11}$ | 44 <sup>1</sup> | $\bullet OH + HO_2^- \rightarrow H_2O + O_2^{\bullet-}$                                            | $8.18 \cdot 10^{10}$ |
| 16 <sup>2</sup> | $H^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^-$                        | $2.73 \cdot 10^{11}$ | 45 <sup>3</sup> | $\bullet OH + HO_2^- \rightarrow HO_2^{\bullet} + OH^-$                                            | $1.24 \cdot 10^{11}$ |
| 17 <sup>2</sup> | $\bullet OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$                  | $4.35 \cdot 10^8$    | 46 <sup>1</sup> | $O^{\bullet-} + H_2O_2 \rightarrow OH^- + HO_2^{\bullet}$                                          | $8.18 \cdot 10^{10}$ |
| 18 <sup>2</sup> | $\bullet OH + O_2^{\bullet-} \rightarrow O_2 + OH^-$                     | $2.07 \cdot 10^{11}$ | 47 <sup>1</sup> | $O^{\bullet-} + HO_2^- \rightarrow OH^- + O_2^{\bullet-}$                                          | $8.76 \cdot 10^{10}$ |
| 19 <sup>2</sup> | $\bullet OH + HO_2^{\bullet} \rightarrow O_2 + H_2O$                     | $7.48 \cdot 10^{10}$ | 48 <sup>1</sup> | $O^{\bullet-} + H_2 \rightarrow OH^- + H^{\bullet}$                                                | $1.55 \cdot 10^9$    |
| 20 <sup>2</sup> | $HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$               | $4.51 \cdot 10^7$    | 49 <sup>1</sup> | $O^{\bullet-} + O_2 \rightarrow O_3^{\bullet-}$                                                    | $3.26 \cdot 10^{10}$ |
| 21 <sup>3</sup> | $HO_2^{\bullet} + O_2^{\bullet-} \rightarrow HO_2^- + O_2$               | $4.31 \cdot 10^8$    | 50 <sup>1</sup> | $O_3^{\bullet-} \rightarrow O^{\bullet-} + O_2$                                                    | $1.99 \cdot 10^7$    |
| 22 <sup>1</sup> | $H_2O_2 \rightarrow 0.5O_2 + H_2O$                                       | $3.78 \cdot 10^{-2}$ | 51 <sup>3</sup> | $O^{\bullet-} + \bullet OH \rightarrow HO_2^{\bullet}$                                             | $2.98 \cdot 10^{11}$ |
| 23 <sup>1</sup> | $H_2O_2 \rightarrow 2\bullet OH$                                         | $3.78 \cdot 10^{-2}$ | 52 <sup>3</sup> | $e_{aq}^{\bullet-} + HO_2^- \rightarrow O^{\bullet-} + OH^-$                                       | $5.79 \cdot 10^{10}$ |
| 24 <sup>1</sup> | $H^+ + OH^- \rightarrow H_2O$                                            | $1.13 \cdot 10^{12}$ | 53 <sup>5</sup> | $e_{aq}^{\bullet-} + HO_2^- \xrightarrow{+H_2O} \bullet OH + 2OH^-$                                | $7.12 \cdot 10^8$    |
| 25 <sup>1</sup> | $H_2O \rightarrow H^+ + OH^-$                                            | $6.52 \cdot 10^{-2}$ | 54 <sup>3</sup> | $O_2^{\bullet-} + HO_2^{\bullet} \rightarrow O_2 + HO_2^-$                                         | $4.31 \cdot 10^8$    |
| 26 <sup>1</sup> | $O_3^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$                        | $5.69 \cdot 10^{11}$ | 55 <sup>3</sup> | $H_2O_2 \rightarrow O^{\bullet} + H_2O$                                                            | $1.02 \cdot 10^{-2}$ |
| 27 <sup>1</sup> | $HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+$                        | $1.55 \cdot 10^5$    | 56 <sup>3</sup> | $O^{\bullet} + O^{\bullet} \rightarrow O_2$                                                        | $8.28 \cdot 10^{10}$ |
| 28 <sup>1</sup> | $\bullet OH + OH^- \rightarrow O^{\bullet-} + H_2O$                      | $1.36 \cdot 10^{11}$ | 57 <sup>6</sup> | $e_{aq}^{\bullet-} + e_{aq}^{\bullet-} \xrightarrow{+H_2O} e_{aq}^{\bullet-} + H^{\bullet} + OH^-$ | $1.99 \cdot 10^{11}$ |
| 29 <sup>1</sup> | $O^{\bullet-} + H_2O \rightarrow \bullet OH + OH^-$                      | $1.76 \cdot 10^8$    |                 |                                                                                                    |                      |

<sup>1</sup> Temperature dependence recommend in ref. [16]. <sup>2</sup> Average of the values reported in refs. [15,16]. <sup>3</sup> Temperature dependence recommend in ref. [15]. <sup>4</sup> Temperature dependence reported in ref. [22]. <sup>5</sup> Value from ref. [25] extrapolated to 300 °C. <sup>6</sup> Temperature dependence from ref. [26].

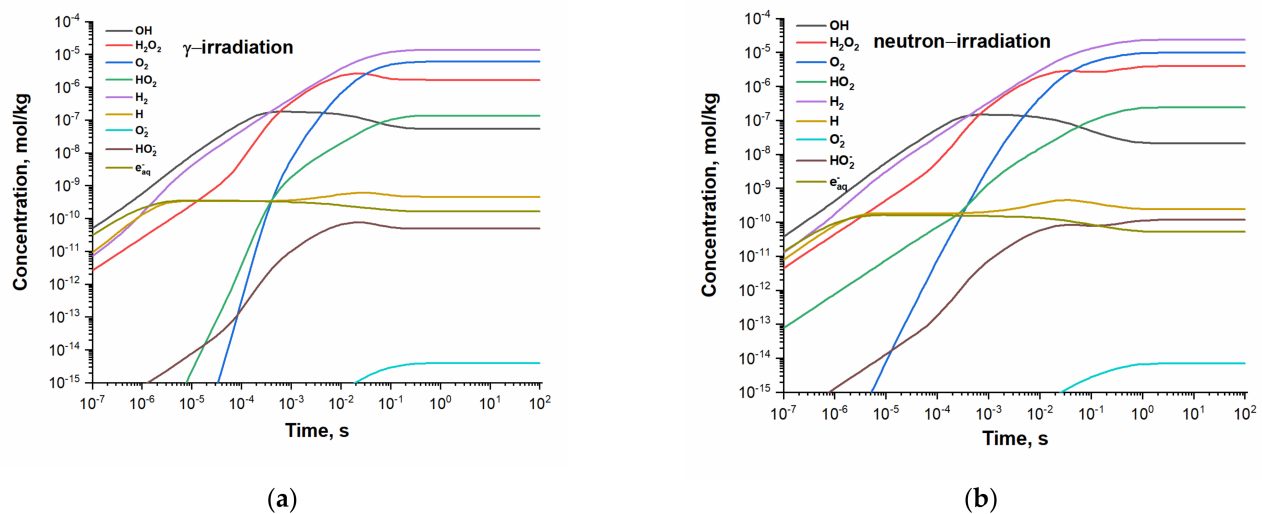
In order to obtain steady-state concentrations, the system of differential equations was numerically integrated up to the time limit  $t_{\max} = 100$  s using the FACSIMILE 4 (ver. 4.2.50, MCPA Software, Harwell, UK) package. Except for  $H_2O$ ,  $H^+$ , and  $OH^-$ , the initial concentration of the reactants was set to zero. The molar concentration of  $H_2O$  was calculated using the density of water at 300 °C,  $0.72 \text{ kg} \cdot \text{dm}^{-3}$ . The initial concentration for  $H^+$  and  $OH^-$ , were obtained from the relation  $pK_w = pH + pOH$ , where  $pK_w$ , expressed in molar units, equals 11.64 at 300 °C [16].

### 3. Results

The results of the kinetic simulations presented here were obtained for neutral water and for an alkaline solution containing  $2 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$  LiOH using the reaction scheme and the rate constants from Table 2.

Concentration profiles of the radiolytic species shown in Figure 1 indicate that the steady state is reached after ca. 10 s. Within 10 and 100 s, the relative change in species concentration is less than 0.08%.

The main species responsible for the formation of oxidising environment are oxygen and hydrogen peroxide. The steady-state concentrations of  $\bullet OH$  and  $HO_2^{\bullet}$  are lower by about two orders of magnitude.

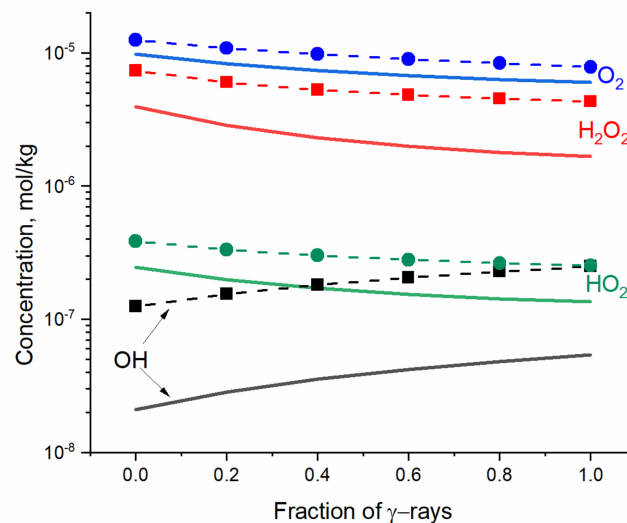


**Figure 1.** Concentration profiles of the radiolytic species calculated for neutral deaerated water exposed to (a) gamma and (b) fast neutron radiation at 300 °C and dose rate 1 kGy·s<sup>−1</sup>.

### 3.1. Main Oxidant Production versus Radiation Composition

#### 3.1.1. Neutral Water

Figure 2 shows the steady-state concentrations of  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\bullet\text{OH}$ , and  $\text{HO}_2^{\bullet}$  as a function of the fraction of  $\gamma$  rays ( $f_g$ ) in the mixed gamma–neutron radiolysis of neutral water.



**Figure 2.** The simulated steady-state concentrations of oxidants formed in neutral water vs. fraction of  $\gamma$ -rays ( $f_g$ ) in the mixed gamma–fast neutron radiation: solid lines indicate dose rate of 1 kGy·s<sup>−1</sup>; dashed + symbol indicates 10 kGy·s<sup>−1</sup>.

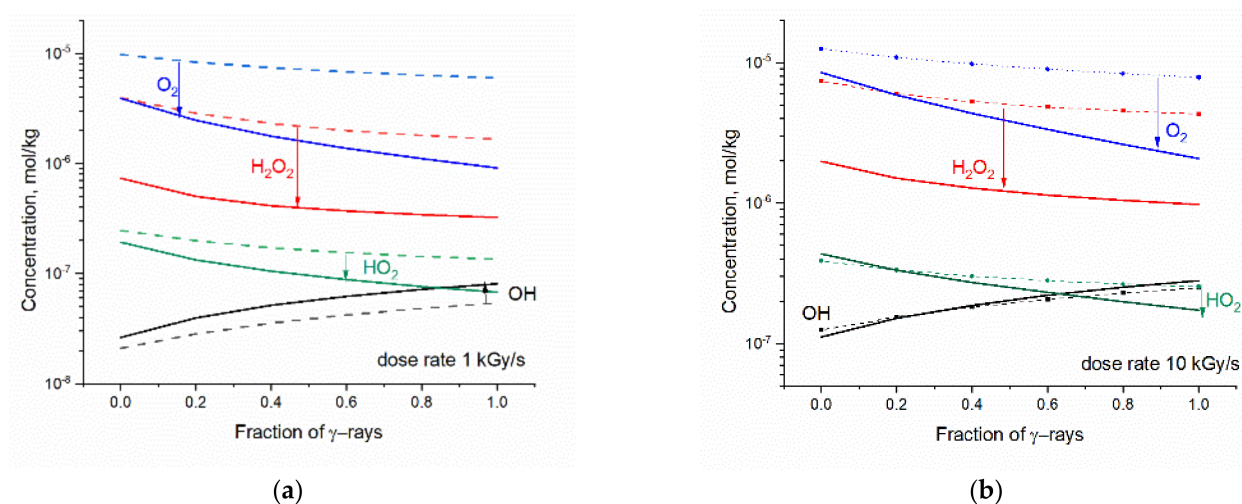
The steady-state concentrations of  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{HO}_2^{\bullet}$ , obtained for fast neutron radiolysis ( $f_g = 0$ ), are higher than the concentration of  $\bullet\text{OH}$ . The increasing fraction of  $\gamma$  rays decreases the concentrations of the molecular oxidants but increases the concentration of  $\bullet\text{OH}$ . This trend is expected since the flux of 2 MeV neutrons produces recoil protons of mean linear energy transfer (LET) 20, 27, 34.5, and 44 eV·nm<sup>−1</sup> [16], whereas  $\gamma$  rays are representative for low-LET radiation (LET~0.2 eV·nm<sup>−1</sup>), producing higher yields of radical than molecular radiolytic products. The number of generated oxidants depends on the dose rate. A particularly significant increase with increasing dose rate was obtained for  $\bullet\text{OH}$  and  $\text{H}_2\text{O}_2$ .

The hybrid method allows one to assess the change in pH under exposure to ionising radiation. The simulation showed a slight decrease in pH, which is more pronounced for

fast neutron radiation—namely, the 100 s exposure to fast neutrons leads to a decline in pH by 0.0023 at the radiation dose of  $1 \text{ kGy} \cdot \text{s}^{-1}$  and by 0.0039 at  $10 \text{ kGy} \cdot \text{s}^{-1}$ , whereas exposure to  $\gamma$  rays leads to a decline in pH by 0.0013 at  $1 \text{ kGy} \cdot \text{s}^{-1}$  and by 0.0028 at  $10 \text{ kGy} \cdot \text{s}^{-1}$ .

### 3.1.2. Alkaline Aqueous Solution

In comparison with neutral water, radiolysis of alkaline solution results in lower steady-state concentrations of  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{HO}_2^\bullet$ ,  $\text{H}_2$ ,  $\text{H}^\bullet$ , and  $\text{O}_2^{\bullet-}$  but in the higher concentrations of  $\text{e}_{\text{aq}}^{\bullet-}$ ,  $^\bullet\text{OH}$ , and  $\text{HO}_2^-$ . Figure 3 presents how the addition of base alters the steady-state concentrations of  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $^\bullet\text{OH}$ , and  $\text{HO}_2^\bullet$  in the mixed gamma–neutron radiolysis. Simulations were performed for fraction of  $\gamma$  rays varying from  $f_g = 0$  (high LET neutron radiolysis) to  $f_g = 1$  (low-LET gamma radiolysis).



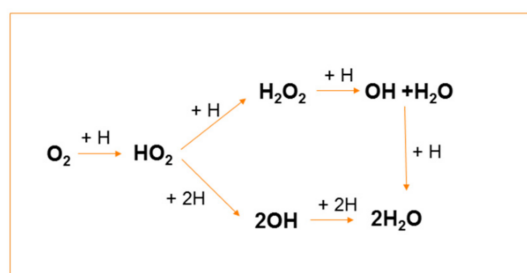
**Figure 3.** Simulated changes in the steady-state concentrations of oxidants resulting from base addition vs. fraction of  $\gamma$ -rays in the mixed gamma–fast neutron radiation: (a) dose rate  $1 \text{ kGy} \cdot \text{s}^{-1}$ ; (b) dose rate  $10 \text{ kGy} \cdot \text{s}^{-1}$ . The solid and dashed lines refer to  $2 \cdot 10^{-4} \text{ mol kg}^{-1}$  LiOH aqueous solution and to neutral water, respectively. The direction of changes is marked by arrows.

In the alkaline solution, the steady-state concentration of stable oxidants is significantly reduced. A change in  $\text{O}_2$  concentration is more pronounced at the dose rate  $1 \text{ kGy} \cdot \text{s}^{-1}$  and develops with increasing  $f_g$ . Simulation shows the decrease by 60% and 85%, respectively, for fast neutron ( $f_g = 0$ ) and gamma ( $f_g = 1$ ) radiolysis at  $1 \text{ kGy} \cdot \text{s}^{-1}$ , compared to 32% ( $f_g = 0$ ) and 74% ( $f_g = 1$ ) at  $10 \text{ kGy} \cdot \text{s}^{-1}$ . In contrast to  $\text{O}_2$ , the decrease in the concentration of  $\text{H}_2\text{O}_2$  is not very sensitive to either radiation composition or dose rate. At a smaller dose rate, the amount of  $\text{H}_2\text{O}_2$  drops by 81%. At  $10 \text{ kGy} \cdot \text{s}^{-1}$ , decreases by 73% and 77% were obtained for  $f_g = 0$  and  $f_g = 1$ , respectively.

Steady-state concentrations of  $\text{HO}_2^\bullet$  and  $^\bullet\text{OH}$  are less sensitive to the addition of base. At  $1 \text{ kGy} \cdot \text{s}^{-1}$ , a decrease in  $[\text{HO}_2^\bullet]$  but an increase in  $[\text{OH}^\bullet]$  by 25% and 50% were obtained for  $f_g = 0$  and  $f_g = 1$ , respectively. Taking into account that the concentration  $^\bullet\text{OH}$  is by several orders of magnitude lower, the overall number of oxidants in the alkaline solution is greatly diminished.

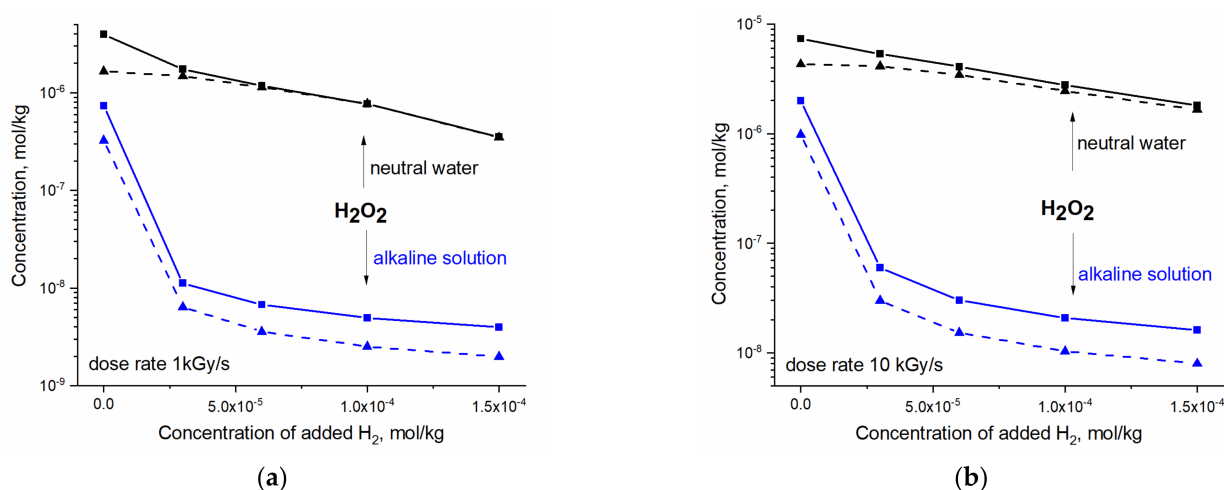
### 3.2. Effectiveness of Hydrogen Addition in Suppressing Production of Stable Oxidants

Molecular hydrogen is one of the reducing products of water radiolysis, but the amount of radiolytic  $\text{H}_2$  is not enough to suppress the formation of stable oxidants. Therefore, to change the oxidising conditions into the reducing ones, hydrogen gas was injected into the coolant. Hydrogen injection promotes reaction (43), converting  $^\bullet\text{OH}$  into the reducing  $\text{H}^\bullet$  radical atom, which initiates the transformation of  $\text{O}_2$  to  $\text{H}_2\text{O}$  in a sequence of reactions, as illustrated in Scheme 2.



**Scheme 2.** Sequence of hydrogen atom reactions leading to conversion of  $O_2$  into  $H_2O$ .

Numerical simulations were performed for fast neutron and gamma radiolysis of neutral water and the alkaline solution ( $2 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \text{ OH}^-$ ). The initial concentration of added  $H_2$  varied from zero (no hydrogen added) to  $1.5 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ . In Figure 4, the calculated steady concentration of  $H_2O_2$  is presented as a function of the amount of added  $H_2$  for the dose rate (a)  $1 \text{ kGy} \cdot \text{s}^{-1}$  and (b)  $10 \text{ kGy} \cdot \text{s}^{-1}$ .

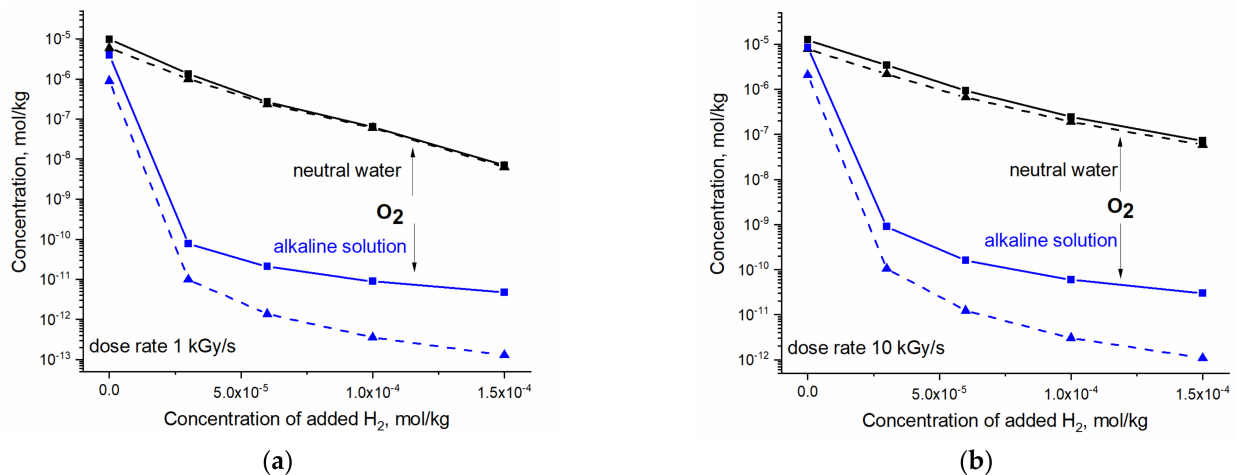


**Figure 4.** Simulated response of the steady-state concentration of  $H_2O_2$  to hydrogen addition to neutral water at  $300^\circ \text{C}$  (black) and to the alkaline solution containing  $2 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \text{ OH}^-$  ions (blue): (a) dose rate  $1 \text{ kGy} \cdot \text{s}^{-1}$ ; (b) dose rate  $10 \text{ kGy} \cdot \text{s}^{-1}$ . Solid and dashed lines refer to fast neutron and gamma radiolysis, respectively.

Simulation shows that the addition of  $H_2$  to the alkaline solution results in a very significant decrease in  $[H_2O_2]$ . This synergistic effect of  $H_2$  and  $\text{OH}^-$  can be expected even at a small concentration of added hydrogen. The reduction in  $H_2O_2$  is not very sensitive to LET and dose rate.

The steady concentration of  $O_2$  calculated vs. the increasing amount of  $H_2$  is presented in Figure 5. Compared with  $H_2O_2$ , the concentration of  $O_2$  responds significantly more to the amount of added  $H_2$ . The reduction in  $O_2$  in neutral water is not very sensitive to LET and dose rate. In the case of alkaline solution, the synergistic effect of  $H_2$  and  $\text{OH}^-$  is more pronounced for gamma radiolysis.

In Table 3, the effectiveness of hydrogen injection is expressed by a ratio of the steady-state concentration of  $H_2O_2$  and  $O_2$  in the absence of extra hydrogen and in the presence of  $1.5 \cdot 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \text{ H}_2$ . Data are shown as a function of dose rate ( $1$  and  $10 \text{ kGy} \cdot \text{s}^{-1}$ ), LET (fast neutron and gamma radiation), and pH (neutral and alkaline water at  $300^\circ \text{C}$ ). An increase in pH enhances the reducing effect of  $H_2$ . The influence of pH is slightly more pronounced at the higher dose rate and lower LET.



**Figure 5.** Simulated response of the steady-state concentration of  $O_2$  to hydrogen added to neutral water at  $300\text{ }^{\circ}\text{C}$  (black) and to alkaline solution containing  $2 \cdot 10^{-4}\text{ mol kg}^{-1}\text{ OH}^{-}$  ions (blue): (a) dose rate  $1\text{ kGy}\cdot\text{s}^{-1}$ ; (b) dose rate  $10\text{ kGy}\cdot\text{s}^{-1}$ . Solid and dashed lines refer to fast neutron and gamma radiolysis, respectively.

**Table 3.** Effectiveness of hydrogen addition expressed as a ratio of the steady-state concentration in the absence of extra hydrogen and in the solution containing  $1.5 \cdot 10^{-4}\text{ mol}\cdot\text{kg}^{-1}\text{ H}_2$ .

| Oxidant/Solution   | $1\text{ kGy}\cdot\text{s}^{-1}$ |                      | $10\text{ kGy}\cdot\text{s}^{-1}$ |                      |
|--------------------|----------------------------------|----------------------|-----------------------------------|----------------------|
|                    | Neutron                          | $\gamma$ -Radiolysis | Neutron                           | $\gamma$ -Radiolysis |
| $H_2O_2$ /neutral  | $1.1 \cdot 10^1$                 | $4.8 \cdot 10^0$     | $4.1 \cdot 10^0$                  | $2.6 \cdot 10^0$     |
| $H_2O_2$ /alkaline | $1.9 \cdot 10^2$                 | $1.6 \cdot 10^2$     | $1.2 \cdot 10^2$                  | $1.2 \cdot 10^2$     |
| $O_2$ /neutral     | $1.4 \cdot 10^3$                 | $9.4 \cdot 10^2$     | $1.7 \cdot 10^2$                  | $1.3 \cdot 10^2$     |
| $O_2$ /alkaline    | $8.2 \cdot 10^5$                 | $7.0 \cdot 10^6$     | $2.8 \cdot 10^5$                  | $1.9 \cdot 10^6$     |

#### 4. Discussion

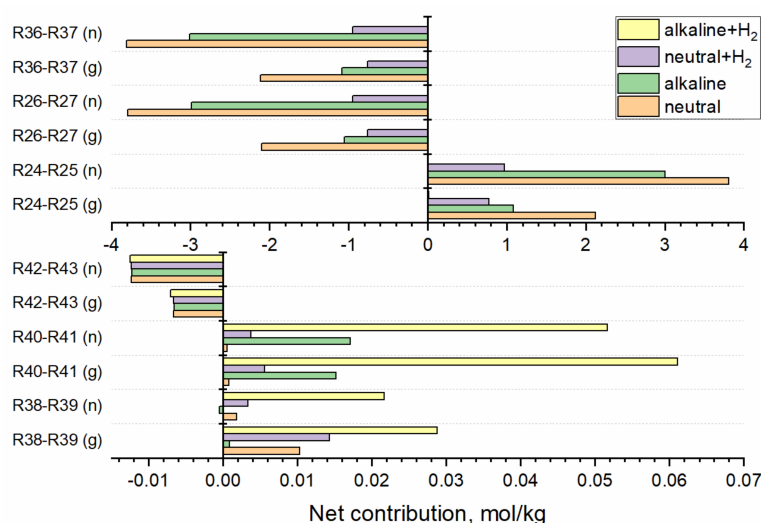
The reaction schemes assumed for simulation by different groups vary at some points. To account for the different values of reported rate constants, the arithmetic mean was assumed as indicated in Table 2, and the following reactions were considered as parallel reactions: (1) and (57); (9) and (10); (14) and (15); (22), (23) and (55); (44) and (45); (52) and (53). The sensitivity of the results to the reaction scheme is discussed below.

##### 4.1. Significance of Reactions

The significance of reactions was assessed based on the integrated (up to 100 s) contributions  $R$  of individual reactions, expressed in  $\text{mol}\cdot\text{kg}^{-1}$ . Reactions contributing in less than  $1 \cdot 10^{-4}\text{ mol}\cdot\text{kg}^{-1}$ , which is the lowest integrated production rate at  $1\text{ kGy}\cdot\text{s}^{-1}$  (Table 1), were considered insignificant. Simulation performed for the dose rate  $1\text{ kGy}\cdot\text{s}^{-1}$  showed that skipping reactions (1), (9), (10), (16), (18), (21), (22), (47), and (52) results in a relative error of the steady-state concentrations of radiolytic products below 0.1%, for all the systems studied. Reactions (2), (23), (55), (56) are slightly more important, but their integrated contributions are of the order of  $10^{-5}\text{ mol}\cdot\text{kg}^{-1}$ .

The most significant are equilibrium reactions, but the assessment of their importance should take into account a net contribution of each equilibrium, expressed as a difference between the integrated contributions of forwarding and backward reactions. Figure 6 shows net contributions calculated for neutral water, alkaline solution, neutral and alkaline solutions containing  $3 \cdot 10^{-5}\text{ mol}\cdot\text{kg}^{-1}\text{ H}_2$ . The upper part presents net contributions R24-R25, R26-R27, R36-R37 of equilibria (24)  $\leftrightarrow$  (25), (26)  $\leftrightarrow$  (27), (36)  $\leftrightarrow$  (37), obtained for gamma and fast neutron irradiation, whereas the lower part refers to equilibria (38)  $\leftrightarrow$  (39), (40)  $\leftrightarrow$  (41), (42)  $\leftrightarrow$  (43), which net contributions are two orders of magnitude smaller. Net

contributions R28-R29, R30-R31, R32-R33, R34-R35, R49-R50, not shown in the figure, are of the order of  $10^{-7}$ – $10^{-4}$  mol·kg $^{-1}$ .

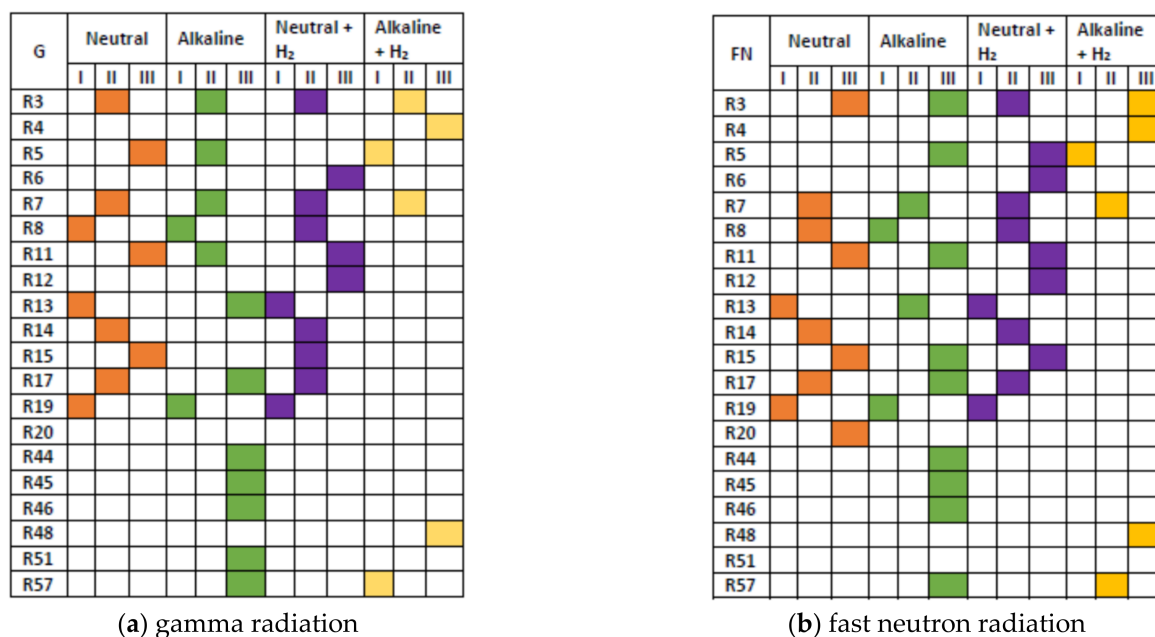


**Figure 6.** Net contributions of equilibria reactions calculated for 1 kGy·s $^{-1}$  fast neutron (n) and gamma (g) radiolysis of neutral water, alkaline solution, and hydrogenated ( $3 \cdot 10^{-5}$  mol·kg $^{-1}$  H $_2$ ) neutral and alkaline systems. Equilibria resulting in net contribution below  $1 \cdot 10^{-3}$  mol·kg $^{-1}$  are not shown.

Equilibrium (24)  $\leftrightarrow$  (25) is shifted to the right, whereas equilibria (26)  $\leftrightarrow$  (27) and (36)  $\leftrightarrow$  (37) are shifted to the left. The net contributions of these equilibria increase with LET and are decreased by the addition of base and H $_2$ . In the alkaline solution containing  $3 \cdot 10^{-5}$  mol·kg $^{-1}$  H $_2$  net contribution of these equilibria is less than  $1 \cdot 10^{-3}$  mol·kg $^{-1}$ , whereas the right shifts of equilibria (40)  $\leftrightarrow$  (41) and (38)  $\leftrightarrow$  (39) obtained for this system are highly increased. The net contribution of right-shifted equilibrium (42)  $\leftrightarrow$  (43) is almost independent of the composition of the solution and more meaningful in the systems irradiated by fast neutrons.

The importance of other reactions is revealed in Scheme 3. The contributions, integrated up to 100 s, were classified into the following three categories: (I)  $1 \cdot 10^{-2} \leq R < 1 \cdot 10^{-1}$  mol·kg $^{-1}$ ; (II)  $1 \cdot 10^{-3} \leq R < 1 \cdot 10^{-2}$  mol·kg $^{-1}$ ; (III)  $1 \cdot 10^{-4} \leq R < 1 \cdot 10^{-3}$  mol·kg $^{-1}$ .

Compared with neutral water, the significance of reactions initiated by  $e_{aq}^{\bullet-}$ , and the alkaline forms of  $\bullet$ OH and HO $_2^{\bullet}$ , i.e., O $^{\bullet-}$  and HO $_2^-$ , is noticeably increased in the alkaline solution, whereas the increase in R6 and R12 seen for neutral hydrogenated system indicates more efficient scavenging of  $\bullet$ OH and H $_2$ O $_2$  by H $^{\bullet}$  in this system. The radiation chemistry of the alkaline hydrogenated solution is controlled by six reactions: (3), (4), (5), (7), (48), and (57). This is a consequence of significant right shifts of equilibria (40)  $\leftrightarrow$  (41) and (38)  $\leftrightarrow$  (39) (Figure 6). In irradiated alkaline hydrogenated solutions, the reducing conditions are maintained by simultaneous production of  $e_{aq}^{\bullet-}$  and H $^{\bullet}$ .



**Scheme 3.** Graphical presentation of importance of reactions from Table 2. The integrated contributions  $R$  were classified into categories I, II, and III, defined in the text above the scheme. Colours correspond to neutral water (orange), alkaline solution (green), and hydrogenated ( $3 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1} \text{ H}_2$ ) systems: neutral (violet) and alkaline (yellow). Based on the simulation carried out for  $1 \text{ kGy} \cdot \text{s}^{-1}$ .

#### 4.2. Key Reactions Contributing to Production of Oxidants

The simulations carried out in this study confirm that  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  are the main radiolytic products responsible for the formation of the oxidising environment in the coolant. The contributions of key reactions leading to the formation and decay of these oxidants in fast neutron (n) and gamma (g) radiolysis of neutral water and the alkaline solution are presented in Figures 7 and 8. The action of added hydrogen is shown for  $[\text{H}_2] = 3 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$ . Contributions of all reactions were integrated up to 100 s.

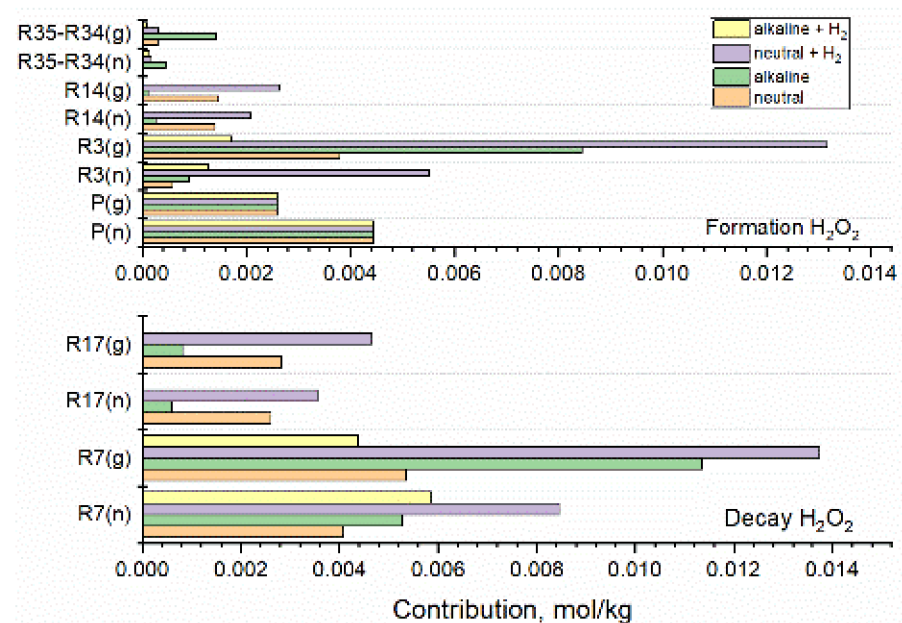
Exposition of the coolant to ionising radiation results in the continuous production of  $\text{H}_2\text{O}_2$  in zeroth-order reactions. In Figure 7, integrated production rates are represented by  $P(g)$  and  $P(n)$ . Since the production rate of  $\text{H}_2\text{O}_2$  by fast neutrons is higher (Table 1),  $P(n)$  exceeds  $P(g)$ . At the small concentrations of base and  $\text{H}_2$ , considered here, the production of  $\text{H}_2\text{O}_2$  is independent of the composition of the irradiated system. Apart from the production, the formation of  $\text{H}_2\text{O}_2$  is controlled by reactions (3), (14), (35), while reactions (7), (17), (34) determine the decay of  $\text{H}_2\text{O}_2$ . Since the contribution of reaction (35) prevails, the net contribution  $R35-R34$  is shown in the upper panel. This net contribution is only relevant for the gamma radiolysis of alkaline solution. Production  $P(n)$  is the most important source of  $\text{H}_2\text{O}_2$  in fast neutron radiolysis of neutral water, whereas  $P(g)$ ,  $R3(g)$ , and  $R14(g)$  are comparable. Contribution  $R14(g)$  is highly increased by  $\text{H}_2$  injection to neutral water but minimised in the presence of a base.

The enormous increase in  $R3(g)$  observed for the alkaline solution and neutral hydrogenated system is balanced by the decay of  $\text{H}_2\text{O}_2$  in reaction with the radicals,  $e_{aq}^{\bullet-}$  and  $\cdot\text{OH}$ . The synergic effect of  $\text{H}_2$  and  $\text{OH}^-$  is seen in the diminishment of  $R3(g)$  obtained for the alkaline hydrogenated solution.

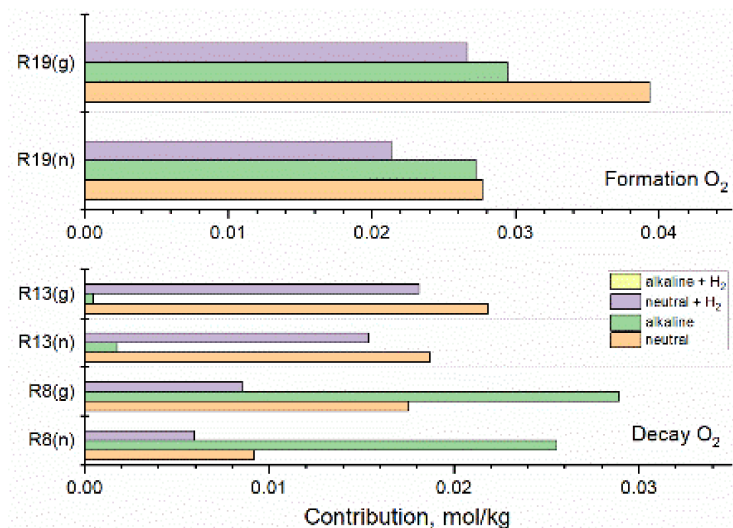
Contributions of key reactions directly responsible for the formation and decay of  $\text{O}_2$  are displayed in Figure 8.

In neutral and neutrally hydrogenated systems,  $\text{O}_2$  decays in reaction (13), producing  $\text{HO}_2^\bullet$ , which reforms  $\text{O}_2$  in reaction (19) with  $\cdot\text{OH}$ . The restoration of  $\text{O}_2$  is less productive in the hydrogenated system, thus diminishing the concentration of  $\text{O}_2$  (Figure 5). In the alkaline solution,  $\text{O}_2$  is produced in reaction (19) but effectively scavenged by  $e_{aq}^{\bullet-}$  in

reaction (8). In the alkaline hydrogenated system, R19(g) and R19(n) are of the order of  $10^{-6}$  and  $10^{-5}$  mol·kg $^{-1}$ , respectively, and the formation of O $_2$  is suppressed.



**Figure 7.** Integrated contributions of key reactions responsible for the formation and decay of H $_2$ O $_2$  calculated for fast neutron (n) and gamma (g) radiolysis of neutral water, alkaline solution, and hydrogenated ( $3 \cdot 10^{-5}$  mol·kg $^{-1}$  H $_2$ ) neutral and alkaline systems. Integrated production rates are represented by P(g) and P(n). Based on the simulation for 1 kGy·s $^{-1}$ .



**Figure 8.** Contribution of key reactions responsible for the formation and decay of O $_2$  calculated for fast neutron (n) and gamma (g) radiolysis of neutral water, alkaline solution, and hydrogenated ( $3 \cdot 10^{-5}$  mol·kg $^{-1}$  H $_2$ ) neutral and alkaline systems. Based on the simulation for 1 kGy·s $^{-1}$ .

## 5. Conclusions

Simulation of water chemistry at 300 °C and under exposure to ionising radiation was performed using the hybrid method [14] and the measured rate constant of  $H^{\bullet} + H_2O \rightarrow \bullet OH + H_2$  reaction [22]. The steady-state concentration of oxidants (O $_2$ , H $_2$ O $_2$ , HO $_2^{\bullet}$ ,  $\bullet OH$ ) were calculated for neutral water (pH $_{573K}$  = 5.8) and an alkaline solution (pH $_{573K}$  = 8.0), as a function of added hydrogen ( $0 \leq [H_2] \leq 1.5 \cdot 10^{-4}$  mol·kg $^{-1}$ ), dose rate (1 and 10 kGy·s $^{-1}$ ), and the fraction of  $\gamma$  rays ( $0 \leq f_g \leq 1$ ) in the mixed fast neutron–gamma radiation. The concentration of main oxidants (O $_2$ , H $_2$ O $_2$ ) increases with the dose rate but

decreases with the increasing fraction of  $\gamma$  rays. At higher pH the total amount of  $O_2$ ,  $H_2O_2$  is significantly diminished. The simulation indicates that the addition of  $H_2$  to the alkaline solution effectively suppresses the formation of oxidising environment. This synergic effect of  $H_2$  and  $OH^-$  may lower CHC.

The importance of reactions contributing to the coolant radiolysis (Table 2) by fast neutrons and  $\gamma$  rays were discussed for neutral, deaerated water and the alkaline solution, and both of these systems contained  $3 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1} H_2$ .

The synergic effect of hydrogen gas and base added to the coolant, demonstrated in this study, provides an important guideline for the development of more efficient methods for controlling the oxidising environment and minimising corrosion problems in PWR engineering.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Acknowledgments:** The author thanks Lukasz Kazmierczak for collecting the literature data on reaction rate constants.

**Conflicts of Interest:** The author declares no conflict of interest.

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