Modelling the radiolysis of RSG-GAS primary cooling water

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Abstract. Water chemistry control for light water coolant reactor required a reliable understanding of radiolysis effect in mitigating corrosion and degradation of reactor structure material. It is known that oxidator products can promote the corrosion, cracking and hydrogen pickup both in the core and in the associated piping components of the reactor. The objective of this work is to provide the radiolysis model of RSG GAS cooling water and further more to predict the oxidator concentration which can lead to corrosion of reactor material. Direct observations or measurements of the chemistry in and around the high-flux core region of a nuclear reactor are difficult due to the extreme conditions of high temperature, pressure, and mixed radiation fields. For this reason, chemical models and computer simulations of the radiolysis of water under these conditions are an important route of investigation. FACSIMILE were used to calculate the concentration of $O_2$ formed at relatively long-time by the pure water $\gamma$ and neutron irradiation (pH=7) at temperature between 25 and 50 °C. This simulation method is based on a complex chemical reaction kinetic. In this present work, 300 MeV-proton were used to mimic $\gamma$-rays radiolysis and 2 MeV fast neutrons. Concentration of $O_2$ were calculated at $10^6 - 10^6$ s time scale.

Keywords: radiolysis, FACSIMILE, RSG-GAS, fast neutrons, $\gamma$-irradiation.

1. Introduction
RSG-GAS reactor is a multipurpose reactor that is utilized for research and scientific purposes. It is an open pool type reactor and use demineralized light (H$_2$O) water as coolant and neutron moderator at the same time. Primary heat transport system in this reactor operates at 40.5-50.57 °C [1]. Cooling water is circulating in the reactor core, where the radiation fields mix at the Linear Energy Transfer (LET), energy deposited per unit length, typically vary $\sim$0.3 sampai 40-60 keV/µm [2]. Irradiation process results in chemical decomposition of water molecule (radiolysis) which generates to the formation of free radical ($e^{-}_{aq}$, H$^*$, •OH, dan HO$_2$//O$_2$•) and molecular product (H$_2$ dan H$_2$O$_2$), and O$_2$ as well. O$_2$ is a secondary product which can lead to corrosion of reactor component and associated reactor piping [2-5]. Corrosion can escalate operation and maintenance cost, radioactive contamination and radiation risk to the workers. Radiation mechanisms depend on several factors, while appropriate water chemistry plays an important role to suppress corrosion and its consequences to the material. RSG GAS have been operating since 30 years ago, when it attained the criticality at 1987, therefore maintaining material structure is necessary important to extend the life span of reactor.

Reliable understanding on the radiolysis process of reactor coolant is very important to control the reactor water chemistry [7]. There are two important key parameters to assess the chemical effect
of ionizing radiation. Those key parameters are (1) yield or $G$-values for $\gamma$-ray and neutron (number of species formed per unit of absorbed energy) and (2) reaction rate constants of involved reactions between species. It is worth mentioning that $G$-values have important role to predict the oxidator concentration, in this case $O_2$, which can cause corrosion of material.

Direct observation or direct chemical measurement in and around high flux reactor core is difficult to conduct. Besides, there is no normal chemical measurement apparatus which is compatible towards the existing of high neutron flux. For these reasons, computer simulation of radiolysis under those conditions is a useful method. In this research work, FACSIMILE software was used to model the radiolysis mechanism then to calculate the concentration of generated $O_2$. The coolant radiolysis caused by the interaction of $\gamma$-ray and neutron is occurred at the temperature range of 25 up to 50 °C. $G$-values for each ionizing radiation are obtained from the calculation results using Monte Carlo simulation.

This research were conducted to provide the radiolysis model of RSG GAS cooling water, since there is no available information in the literature currently, while plenty of information are available for nuclear power plants. It is considered that radiolysis model of RSG GAS cooling water using FACSIMILE can give the information of $O_2$ concentration which can lead to corrosion of reactor material.

2. Methodology

Radiolysis process causes formation of free radical species, molecular products and chemical reaction between formed species. In this research, batch system continuous irradiations were assumed. Radiolytic species was expected to reach the steady state concentration at longer time relatively to the time scale of homogeneous stage in the radiation interaction. To model this radiolysis, several parameters are needed, such as $G$-values, set of possible reactions, reaction rate constants and dose rate.

Simulation at room temperature (25 °C) should be done at first in order to validate reactions set feeded to the model. It should be done due to the abundant experimental data are exist at room temperature. Then, simulation for temperature above 25 °C were done. Radiolysis simulation is a simultaneously chemical reaction analysis and the effect of multivariable differential as a function of time. In this work, FACSIMILE software was used to integrate differential equations [8]. FACSIMILE software is a powerful modelling tool that is designed to efficiently solve differential equations, with the focus is on modelling the kinetics of physical and chemical systems. There are many benefits of using FACSIMILE such as to model transport and chemistry problems and to develop useful models rapidly with specific facilities for modelling chemical kinetics.

2.1. $G$-values

$G$-values of radiolytic species depend on several factors, such as temperature and LET. To gain the objective of this work, $G$-values of radiolytic species formed by the interaction of $\gamma$-ray and neutron with water at room and higher temperature are required. $G$-values which obtained from Monte Carlo simulation are shown at Table 1.

| Species | $\gamma$-ray [9] | Neutron [10] |
|---------|-----------------|--------------|
|         | 25 °C | 50 °C | 25 °C | 50 °C |
| $e^{-}_{aq}$ | 2.64 | 2.62 | 0.43 | 0.81 |
| $H^{+}$ | 0.57 | 0.64 | 0.58 | 0.59 |
| $OHa$ | 2.82 | 2.84 | 0.93 | 0.98 |
| $H_{2}$ | 0.45 | 0.48 | 1.07 | 0.91 |
| $H_{2}O_{2}$ | 0.65 | 0.63 | 1.11 | 1.05 |
2.2. Reaction rate constants

Reaction rate constants, reaction mechanisms from Atomic Energy of Canada Limited (AECL) compilation report of Elliot and Bartels were used in FACSIMILE [11]. This data base provides the best recommended value to be used in high temperature water radiolysis modelling, at temperature range 20-350 °C.

### Table 2. Main reaction set and reaction rate constants for water radiolysis at room temperature (25 °C)[11]

| Reaction | $k$ (M⁻¹s⁻¹) | Reaction | $k$ (M⁻¹s⁻¹) |
|----------|---------------|----------|---------------|
| H⁺ + H⁺→H₂ | 5.2 × 10⁷ | e⁻aq + e⁻aq→H₂ + 2 OH⁻ | 7.3 × 10⁷ |
| H⁺ + OH⁻→ H₂O | 1.6 × 10¹⁰ | e⁻aq + H⁺→ H²⁺ | 2.1 × 10¹⁰ |
| H⁺ + H₂O₂→ H₂O + OH⁻ | 3.6 × 10⁷ | e⁻aq + O₂⁻→ H₂O₂ + 2 OH⁻ | 1.3 × 10¹⁰ |
| H⁺ + H₂O₂→ H₂ + OH⁻ | 2.8 × 10¹⁰ | e⁻aq + HO₂⁻→ O⁻ + OH⁻ | 3.51 × 10⁹ |
| H⁺ + OH⁻→ H₂O₂ + e⁻aq | 2.4 × 10⁷ | e⁻aq + O⁻→ 2 OH⁻ | 2.31 × 10¹⁰ |
| H⁺ + O₂→ HO₂⁻ | 1.3 × 10¹⁰ | e⁻aq + H₂O→ H⁺ + OH⁻ | 15.8 |
| H⁺ + HO₂⁻→ H₂O₂ | 1.1 × 10¹⁰ | e⁻aq + O₂→ O₂⁻ | 2.3 × 10¹⁰ |
| H⁺ + O₂⁻→ HO₂⁻ | 1.1 × 10¹⁰ | e⁻aq + HO₂⁻→ HO₂⁻ | 1.3 × 10¹⁰ |
| H⁺ + HO₂⁻→ OH⁻ + O₂ | 1.5 × 10⁹ | e⁻aq + O(3P)→ O⁻ | 2.0 × 10¹⁰ |
| H⁺ + O(3P)→OH⁻ | 2.0 × 10⁹ | e⁻aq + O₂→ O₂⁻ | 3.6 × 10¹⁰ |
| H⁺ + O⁻→ OH⁺ | 2.0 × 10¹⁰ | H⁺ + O⁻→ OH⁻ | 5.0 × 10¹⁰ |
| H⁺ + O₂→ O₂ + OH⁻ | 3.7 × 10¹⁰ | H⁺ + O₂→ HO₂⁻ | 5.0 × 10¹⁰ |
| H⁺ + O₂⁻→ OH⁻ + O₂ | 1.0 × 10¹⁰ | H⁺ + OH⁻→ H₂O | 1.2 × 10¹¹ |
| 'OH + 'OH→ H₂O₂ | 6.3 × 10⁹ | H⁺ + O₂→ 'OH+ O₂ | 9.0 × 10¹⁰ |
| 'OH + H₂O₂→ HO₂⁻+ H₂O | 2.9 × 10⁷ | H⁺ + HO₂⁻→ H₂O | 5.0 × 10¹⁰ |
| 'OH + H₂→ H⁺ + H₂O | 4.0 × 10⁷ | OH⁻ + O(3P)→ HO₂⁻ | 4.2 × 10⁸ |
| 'OH + e⁻aq→ OH⁻ | 3.6 × 10¹⁰ | OH⁻ + HO₂⁻→ O₂⁻ + H₂O | 1.3 × 10¹⁰ |
| 'OH + OH⁻→ O²⁻ + H₂O | 1.3 × 10¹⁰ | O₂⁻ + O²⁻→ O₁⁻ | 3.7 × 10⁹ |
| 'OH + HO₂⁻→ O₂ + H₂O | 9.0 × 10⁹ | O₂⁻ + O(3P)→ O₁⁻ | 4.0 × 10⁹ |
| 'OH + O₂⁻→ O₂ + OH⁻ | 1.1 × 10¹⁰ | HO₂⁻ + O₂⁻→ HO₂⁻| 9.7 × 10⁷ |
| 'OH + HO₂⁻→ HO₂⁻ + OH⁻ | 8.3 × 10⁹ | HO₂⁻ + HO₂⁻→ H₂O₂ + O₂ | 1.94 × 10⁸ |
| 'OH + O(3P)→ HO₂⁻ | 2.02 × 10¹⁰ | HO₂⁻ + O(3P)→ O₂⁻ + OH⁻ | 2.02 × 10¹⁰ |
| 'OH + HO₂⁻→ HO₂⁻ | 1.0 × 10⁹ | HO₂⁻ + H₂O→ H⁺ + O₂⁻ | 1.4 × 10⁹ |
| 'OH + O₂⁻→ O₂⁻ + HO₂⁻ | 8.5 × 10⁹ | O₂⁻ + O⁻→ O₂ + 2 OH⁻ | 6.0 × 10⁸ |
| 'OH + O₂⁻→ O₂⁻ + HO₂⁻ | 1.11 × 10¹⁰ | O₂⁻ + H₂O→ HO₂⁻ + OH⁻ | 0.155 |
| H₂O₂ + e⁻aq→ OH⁻ + OH⁺ | 1.1 × 10¹⁰ | O₂⁻ + O₂⁻→ O₁⁻ + O₂ | 1.5 × 10⁹ |
| H₂O₂ + OH⁻→ HO₂⁻ + H₂O | 1.33 × 10¹⁰ | HO₂⁻ + H₂O→ H₂O₂ + OH⁻ | 1.27 × 10⁶ |
| H₂O₂ + O(3P)→ HO₂⁻ + OH⁻ | 1.6 × 10⁹ | HO₂⁻ + O⁻→ O₂⁻ + OH⁻ | 8.02 × 10⁸ |
| H₂O₂ + O²⁻→ HO₂⁻ + OH⁻ | 5.55 × 10⁹ | HO₂⁻ + O(3P)→ O₂⁻ + OH⁻ | 5.3 × 10⁹ |
| H₂ + O(3P)→ H⁺ + 'OH | 4.77 × 10⁴ | O⁻⁻ + O⁻→ H₂O₂ + 2 OH⁻ | 1.0 × 10⁸ |
| H₂ + O²⁻→ H⁺ + OH⁻ | 1.3 × 10⁸ | O⁻⁻ + O₂→ 2 O₂⁻ | 7.0 × 10⁸ |
| O(3P) + O(3P)→ O₂ | 2.2 × 10¹⁰ | O⁻⁻ + H₂O→ OH⁻ + OH⁻ | 1.3 × 10⁹ |
| O(3P) + H₂O→ 2 OH⁻ | 1.9 × 10¹⁰ | O₁⁻→ H₂O→ O⁻⁺ + O₂ | 46.5 |
2.3. Dose rate

Dose rate is one of key parameters to model coolant radiolysis. The following is series of calculations to obtain average dose rate of each radiation type used in this work [12].

2.3.1. γ-ray dose rate

Total gamma sources of RSG-GAS (consist of radioactive capture, spontaneous fission and radioactive decay) in operating condition: 7.91E20 photon/s

Pool area of RSG-GAS:

\[ 2 \times (60 \text{ cm} \times (8 \times 7.71 \text{ cm})) + 2 \times (60 \text{ cm} \times (8 \times 8.1 \text{ cm})) + 2 \times ((8 \times 7.71 \text{ cm}) (8 \times 8.1 \text{ cm})) = 23,171 \text{ cm}^2 \]

γ-ray Flux = 7.91E20 photon/s x (1/23,171 cm²)

Gamma (γ) flux conversion factor towards dose rate = 1.42E-4 (rem/hr)/(photon/cm² s)

Thus, γ-ray dose rate:

\[ = 1.42E-4 \text{ (rem/hr)/( photon/cm}^2 \text{ s)} \times 7.91E20 \text{ photon/s} \times (1/23,171 \text{ cm}^2) \]

\[ = 4.84E12 \text{ rem/hr} \quad ; \text{ if 1 rem} = 0.01 \text{ Gy and 1 hr} = 3600 \text{ s, so that} \]

\[ = 1.34E7 \text{ Gy/s} \]

2.3.2. Neutron dose rate

Flux neutron = 3.34E14 neutron/ cm² s

neutron flux conversion factor towards dose rate = 1.04E-2 (rem/hr)/(neutron/cm² s)

Thus, neutron dose rate:

\[ = 1.04E-2 \text{ (rem/hr)/(neutron/cm}^2 \text{ s)} \times 3.34E14 \text{ neutron/ cm}^2 \text{ s} \]

\[ = 3.48E12 \text{ rem/hr} \quad ; \text{ if 1 rem} = 0.01 \text{ Gy and 1 hr} = 3600 \text{ s, so that} \]

\[ = 9.67E6 \text{ Gy/s} \]

3. Results and Discussion

Modelling the radiolysis of RSG GAS primary cooling water using FACSIMILE software has been conducted. This software has been validated with several calculations at both conditions, neutral and the existing of solution. In order to validate our feeded model, it is necessary to check mass equilibrium and the ratio of hydrogen atom number and oxygen atom number, principally, is about 2:1 [13]. Variation of O₂ concentrations towards time due to interaction of γ-ray and neutron with water are shown in red and blue solid line, respectively in the following figures.

3.1. Simulation at 25°C

Figure 1 shows O₂ concentrations as a function of times that are obtained from our simulation at room temperature (25 °C) and aerated condition (pool type). The behaviour caused by these two radiation types are different. At early time, oxygen concentrations generated by γ-ray and neutron increase until
0.01 s. At this time scale, this phenomenon is due to the aeration condition, where the oxygen content over the pool could diffuse into the coolant. Another hypothesis that could be addressed to elucidate the escalation of \(O_2\) concentrations is the contribution of chemical reactions as follows (the order is based on the high possibility to occur):

\[
e^{-_{\text{aq}}} + O_2 \rightarrow O_2^-
\]
\[
H^+ + O_2 \rightarrow HO_2^-
\]
\[
O_2 + O(^3\text{P}) \rightarrow O_3
\]
\[
O_2 + O^- \rightarrow O_3^-
\]

Those reactions consume \(O_2\) in the water, while the reactions which form \(O_2\) as follows (the order is based on the high possibility to occur):

\[
H^+ + O_3 \rightarrow O_2 + \cdot \text{OH}
\]
\[
\text{HO}_2^\cdot + O(^3\text{P}) \rightarrow O_2 + \cdot \text{OH}
\]
\[
H^+ + O_3^- \rightarrow \text{OH}^+ + O_2
\]
\[
O_2^- + O^- \rightarrow O_2 + 2 \text{OH}^-
\]
\[
\text{HO}_2^\cdot + \text{HO}_2^\cdot \rightarrow \text{H}_2\text{O}_2 + O_2
\]
\[
\text{HO}_2^\cdot + O_2^- \rightarrow \text{HO}_2^- + O_2
\]

The difference between these two ionizing radiations can be observed at time \(> 0.01\) detik.

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**Figure 1.** Variation of \(O_2\) concentration towards time at 25 °C, red solid line for \(\gamma\)-ray interaction and black solid line for neutron interaction.
For γ-ray interaction, O$_2$ concentration reaches the steady state earlier (at time 0.1 s) rather than neutron interaction with water (which is at 100 s). Steady state condition is a condition when there are no more reactions that generate and consume O$_2$. In addition to that, O$_2$ concentration formed by γ-ray interaction with water is lower compared with neutron. It is known that O$_2$ is a secondary molecular product induced by radiolysis. Principally, radiolytic product, in this case free radicals, is found greater for radiolysis induced by γ-ray interaction (low-LET) rather than neutron interaction (high-LET), vice versa for molecular product formation such as O$_2$). This trend is signatur ed by the high-LET characteristic of neutron, itself, in which neutron deposit its energy at higher density as compared to γ-ray.

It is obvious that high LET deposits its energy at the vicinity thus spur/track which consists of free radical will overlap prior to spur/track lifetime. It results in the less free radical formation or in other words more molecular formation. Since there are more than one radiation types, thus oxygen formation will be accumulated.

At the time above 1E-5 s, both radiation types increase the number of oxygen concentration regardless the gap on neutron interaction at time 1s. The gap is induced by the reactions of oxygen consuming which play role at this time, having said that these reactions have relatively low reaction rate constant. Following 10 s later, there is a competition between reaction that consume oxygen and reaction that produce oxygen, from Fig 1, it looks like reactions to produce oxygen are more powerful prior to the steady state condition obtained.

3.2. Simulation at 50 °C

Figure 2 shows O$_2$ concentrations at aerated condition as a function of times as a result of γ-ray and neutron interaction with RSG-GAS cooling water. For γ-ray, O$_2$ concentration decline drastically after 0.01 s and even can be neglected. However for neutron, in contrary O$_2$ concentration increases significantly after 0.001 s after this radiation interacted with coolant. This phenomenon could be due to several reactions are sensitive to the temperature escalation, particularly reactions which form O$_2$ such as (5)-(10).

![Figure 2](image-url)  
Figure 2. Variation of O$_2$ concentration towards time at 50 °C, red solid line for γ-ray interaction and black solid line for neutron interaction.
For γ-ray interaction, it looks like oxygen formation decrease significantly after 0.01 s. It can be confirmed that oxygen consuming reactions compete over the oxygen generating reactions. The opposite phenomenon is occured to the neutron interaction, where oxygen number increases as a function of time. However, a comprehensive investigation, especially at longer time, is required related to reactions behaviour towards the temperature above room temperature and radiation flux measurement. These important data will certainly give a clear model of coolant radiolysis. Moreover, the consequences of the radiolysis of coolant towards reactor component can be predicted, take into account that this reactor has been operated for about 30 years.

4. Conclusion
In this research work, FACSIMILE was used to model radiolysis of RSG GAS cooling water in order to calculate O₂ concentration as a result of γ-ray and neutron interaction at temperature 25 and 50 °C. At 25 °C, O₂ concentration was calculated until it can reach the steady state condition at time between 10⁻⁶ and 10⁵ s. For γ-ray interaction, O₂ concentration reaches steady state at earlier time (at time 0.1 s) as compared to neutron interaction (at time 100 s). O₂ concentration formed by gamma is lower than neutron. At 50 °C, O₂ concentration as a result of γ-ray decreases drastically after 0.01 s and even can be neglected, however the contrary behaviour occured to neutron interaction. This phenomenon could be caused by several reactions which are sensitive with the escalation of temperature, therefore a comprehensive investigation are neccessary required. Moreover, to test our model and calculation, experimental data and measurement are needed.

Acknowledgment
The authors are wishing to thank national project fund (DIPA) of Center for Nuclear Reactor Technology and Safety, BATAN, year 2016 and Mr. Amir Hamzah for the valuable data and discussion regarding research reactor.

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