

Conference Paper

The Effect of Hydrazine Addition on the Formation of Oxygen Molecule by Fast Neutron Radiolysis

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Abstract

Hypothetically speaking, hydrazine could suppress the oxygen formation as a major of corrosion initiator. In this work, we developed a calculation model to understand the effect of hydrazine addition toward the oxygen under PWR condition. Our great interest is to study whether this strategy would also be effectively applied in PWRs. In the present work, the effect of hydrazine on suppressing the molecule oxygen under neutron irradiation is described. The simulation was done by using FACSIMILE. The variation dose applied assuming a batch system and at high dose $\sim 10^4$ Gy s^{-1} . Three different temperatures were applied, which are room temperature, 250 and 300 °C at two system oxygenated water, which are aeration and deaeration. At room temperature, for deaerated condition, added hydrazine under a range of 10^{-6} – 10^{-4} M into primary coolant were not effective to suppress O_2 form since the effect was similar as in the pure water system since for 10^{-3} M hydrazine addition, a large produce of O_2 were obtained. In reverse, for deaerated condition, hydrazine concentrate about 10^{-3} M can suppress O_2 form significantly, while hydrazine add in the range between 10^{-6} – 10^{-4} M is again confirmed to be the same as in pure water system. For high temperature, at 250 and 300 °C, the results showed that in deaerated condition, hydrazine addition can suppress O_2 form proportionally to its concentration while in aerated condition, hydrazine add with concentration of 10^{-6} and 10^{-5} M were not effectively to suppress O_2 form, a slightly decrease of O_2 occurred due to the addition of 10^{-4} M hydrazine and 10^{-3} M of hydrazine can suppress the formation of O_2 significantly.

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1. Introduction

Pressurized Water Reactors (PWRs) use light water (H_2O) both as a coolant and as a moderator [1]. In the reactor core, water is circulated under extreme conditions such as high pressure, high temperature and heavy mixed neutron/ γ -radiation fields results in chemical decomposition of water (radiolysis) [2]. By means of radiolysis of water, various species such as free radicals (e^-_{aq} , H^\cdot , $\cdot OH$, and HO_2^\cdot/O_2^\cdot) and molecular products (H_2 , H_2O_2 and O_2 (as a secondary product)) are generated continuously. These species can lead to corrosion, cracking, and hydrogen pickup both in the core and in the associated piping components of the reactor [2-5]. As this issue has been an important consideration in PWRs, thus optimal water chemistry control is expected to play important role to mitigate the corrosion caused by radiolysis of water.

Recently, chemical compound being added into primary systems of PWRs such as: 1) dissolved hydrogen to suppress the oxidizing radicals and molecular products formation, 2) boron in form of boric acid to control the neutron reactivity and to suppress the oxygen concentration that play role on corrosion process [6]. While Ishida et al. (2006) have developed a selected method to mitigate stress corrosion cracking in boiling water reactors (BWRs) named hydrazine and hydrogen co-injection (HHC) [7], which is injected through feed water system. Hypothetically speaking, hydrazine could suppress the oxygen formation as a major of corrosion initiator. In this work, we developed a calculation model to understand the effect of hydrazine addition toward the oxygen under PWR condition. Our great interest is to study whether this strategy would also be effectively applied in PWRs.

In this work, FACSIMILE computer code were used to investigate the effect of hydrazine to suppress the oxidator, O_2 , on primary cooling water radiolysis at temperatures between 25 and 350 °C under neutron irradiation. We considered that G-values, the number of species produced (or consumed) per unit of energy absorbed, and rate constant of all species involved that we used in this calculation would be acceptable up to 350 °C. How far is the effects of hydrazine addition toward the formation of oxygen were discussed in this work.

2. Methodology

The absorption of ionizing energy by the coolant results in coolant radiolysis which can generate continuously free radical species and molecular products (where free radical species react with each other). In this study, we assumed a continuous radiation in a homogeneous chemical stage batch system, as coolant radiolysis is categorized in this type. It has been described in detail previously [8] that radiation chemical simulation is an analysis of simultaneous chemical reactions and is in effect the integration of time-dependent multivariable simultaneous differential equations. Therefore, in this present work, FACSIMILE was used to solve differential equations.

The important key parameters to evaluate the chemical effects of ionizing radiation are temperature dependence of the radiation-chemical yields or G-values of the species (in this case for fast neutrons), and the rate constants for all of the reactions involving these species in pure water. These two parameters are needed as inputs for our code. In addition to that, high dose rate of neutrons 10^4 Gy/s, aeration and deaeration system, and the reaction set of a hydrazine system. Details information were discussed as follow.

G-value is given in the units of "molecule per 100 eV"; for conversion into SI units (mol/J), 1 molecule/100 eV \approx 0.10364 μ mol/J. In this work, we need G-values of reactive radical species, molecular product and water itself by fast neutron irradiation. G-value of fast neutrons were taken from Ref. [9] (Table 1), it is a combination of measurements and computer modeling; irradiations carried out using the YAYOI fast-neutron source reactor at the University of Tokyo, with an average energy for fast neutrons of \sim 0.8 MeV. G-values measured at 250 °C were adopted for temperature above 250 °C. In order to provide the reaction set and rate of reaction as one of important parameter for one to understand radiolysis process, we use the self-consistent radiolysis database that recently compiled by Elliot and Bartels [10] (the reactions set not shown in this work). This new database provides recommended values to use in high-temperature modeling of light water radiolysis over the temperature range between 20-350 °C. In addition to that, the reactions set of hydrazine is also necessary in order to know the effect of hydrazine addition. Table 1 provides a numbered list of reactions and corresponding rate constants used in this work. The mechanism reaction of hydrazine with free radicals and molecular products, also with O_2 radicals is quite complex.

TABLE 1: Main chemical reactions of hydrazine and their corresponding rate constants (k) at 25 °C used in our FACSIMILE. For first-order reactions (indicated by the symbol †), the value of k is given in s^{-1} .

Reaction	Symbol	$k(M^{-1}s^{-1})$
R1	$e^-_{aq} + N_2H_5^+ \rightarrow H^\cdot + N_2H_4$	1.60×10^8
R2	$H^\cdot + N_2H_4 \rightarrow H_2 + N_2H_3$	1.30×10^5
R3	$H + N_2H_5^+ \rightarrow H_2 + N_2H_4^+$	1.30×10^5
R4	$OH + N_2H_4 \rightarrow N_2H_3 + H_2O$	5.40×10^9
R5	$OH + N_2H_5^+ \rightarrow N_2H_4^+ + H_2O$	8.20×10^7
R6	$N_2H_4^+ + N_2H_4^+ \rightarrow N_4H_8^{2+}$	1.00×10^8
R7	$N_2H_3 + N_2H_3 \rightarrow N_4H_6$	6.00×10^8
R8	$N_4H_8^{2+} \rightarrow NH_4^+ + N_3H_4^+$	$1.00 \times 10^4 \text{ †}$
R9	$N_4H_6 \rightarrow NH_3 + N_3H_3$	$7.20 \times 10^4 \text{ †}$
R10	$N_2H_4 + H_2O_2 + H_2O_2 \rightarrow N_2 + 4H_2O$	2.43×10^8
R11	$N_2H_3 + H_2O_2 \rightarrow OH + N_2H_2 + H_2O$	1.00×10^9
R12	$N_3H_4^+ \rightarrow N_2 + NH_4^+$	$1.30 \times 10^4 \text{ †}$
R13	$N_2H_4 + O_2 \rightarrow H_2O + H_2O + N_2$	7.00×10^3
R14	$N_2H_3 + O_2 \rightarrow O_2^- + H^\cdot + N_2H_2$	3.80×10^8
R15	$N_2H_2 + N_2H_2 \rightarrow N_2 + N_2H_4$	2.00×10^4
R16	$H^\cdot + N_2H_4 \rightarrow N_2H_5^+$	1.00×10^1
R17	$N_2H_5^+ + H \rightarrow NH_2 + NH_4^+$	1.30×10^5
R18	$H^\cdot + N_2H_3 \rightarrow N_2H_4^+$	1.00×10^1
R19	$N_3H_2^- \rightarrow N_2 + NH_2^-$	$7.70 \times 10^3 \text{ †}$
R20	$OH + NH_3 \rightarrow NH_2 + H_2O$	7.52×10^8
R21	$NH_2 + NH_2 \rightarrow N_2H_4$	1.00×10^{10}
R22	$NH_2 + N_2H_4 \rightarrow N_2H_3 + NH_3$	1.00×10^7
R23	$NH_3 + H \rightarrow NH_4^+ + e^-_{aq}$	7.00×10^6
R24	$H + N_2H_3 \rightarrow N_2H_4$	7.00×10^9
R25	$N_2H_5^+ \rightarrow H^\cdot + N_2H_4$	$7.88 \times 10^2 \text{ †}$
R26	$N_2H_4^+ \rightarrow H^\cdot + N_2H_3$	$7.88 \times 10^3 \text{ †}$
R27	$N_3H_4^+ \rightarrow H^\cdot + N_3H_3$	$1.00 \times 10^1 \text{ †}$

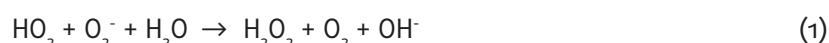
In this work, the concentration of hydrazine added to the system is under a range (10^{-6} to 10^{-3} M) and using a well-accepted mechanism for radiolysis in the presence or absence of air. Dose rate is also one of the input data to perform radiolysis simulation. Dose rate of neutrons are assumed as high dose rate conditions, a typical condition in reactor core (10^4 Gy s^{-1}). Once again, the purpose of this study is to understand the best estimation of hydrazine addition to suppress the O_2 formation in primary coolant water system.

3. Result and Discussion

The effect of hydrazine on coolant radiolysis at temperature range between 25-300 °C, high neutron dose rate condition and in the presence or absence of air were carried out using computer code FACSIMILE. Our code has been validated with other calculation in pure and other solution. The validity of the simulation is checked from the aspect of mass balance and numbers of hydrogen and oxygen atoms in major products are approximately 2:1 [8]. For the sake of comparison, the time evolution of O_2 concentration were calculated in pure water system (black lines) and by varying the concentration of hydrazine added to our system under a range, 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M (magenta, blue, green and red lines, respectively).

1. Simulation at room temperature

Figure 1 shows the time evolution of $[O_2]$ as reproduced by our simulation at 25 °C in deaerated (a) and aerated (b) condition. For deaerated condition, the varying concentration of added hydrazine in the range between 10^{-6} – 10^{-4} M has no effect in reaching the steady state concentration of O_2 which is similar as in the pure water system. However, a striking feature of our simulated results obtained at 10^{-3} M hydrazine addition, where it increases with time, was the large produce of O_2 . Our hypothesis for this result is that there are two reactions contribute to the formation of O_2 (based on the importance) at longer time:



Reaction (2) is much slower with a rate constant about 3 order of magnitude lower than for reaction (1). In reverse the concentration of hydrazine about 10^{-3} M can suppress the formation of O_2 significantly pass through a minimum point then reach the steady state concentration at very low level $\sim 5 \times 10^{-9}$ M, while the addition of hydrazine in the range between 10^{-6} – 10^{-4} M is confirmed in Figure 1(b) as the same as in pure water system.

The results for the concentration of O_2 in aerated aqueous 10^{-3} M hydrazine solutions show that this long-lived molecular species are decreased compared to those in deaerated solutions. The reactions of oxygen consumption, reaction R13 and R14 are much faster than the reactions of oxygen formation such as reaction (1) and (2), thereby cannot protect the oxygen molecule from further reactions with these species in the homogeneous stage of radiolysis, or in other words, this phenomena leads to a decrease in the concentration of O_2 . Indeed, as can be seen in Figure 1, the steady state concentration of O_2 in aerated hydrazine solutions are six magnitudes lower than in deaerated solutions.

2. Simulation at 250 °C and 300 °C

Figure 2(a), (b) and Figure 3(a), (b) show time variations of the oxygen molecule as a function of time in pure water and hydrazine solution at deaerated and aerated condition respectively. Overall, in all case, steady state concentrations of O_2 are lower than those in Figure 1 both in the presence or absence of air. In deaerated condition, Figure 2(a) and Figure 3(a), shows obviously how each concentration of hydrazine addition suppress the formation of O_2 . It is readily explained that the higher the concentration of hydrazine the lower the generation of O_2 . This explanation is described in combination of reaction R.. and R.. that convert the N_2H_4 and N_2H_3 into water, N_2H_2 and N_2 .

In the other side, the highest concentration of hydrazine which is 10^{-3} M can suppress the formation of O_2 until it becomes negligible $\ll 10^{-20}$ M. Figure 2(b) and Figure 3(b) show that in absence of hydrazine addition give the same result with 10^{-6} and 10^{-5} M of hydrazine

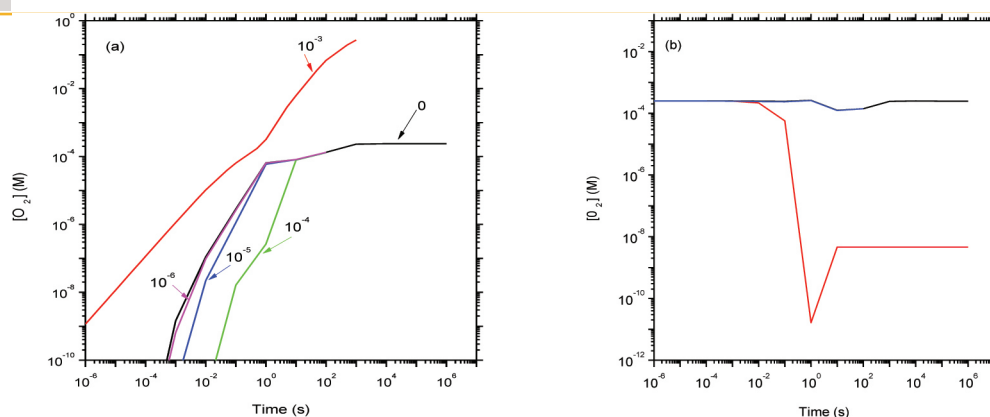


Figure 1: Time evolution of $[O_2]$ (in Molar) of pure water (black lines) and aqueous hydrazine solutions at 25 °C, calculated using our FACSIMILE in deaerated (a) and aerated (b) condition at the assumption of dose rate 10^4 Gy s^{-1} . and by varying the concentration of hydrazine added to our system under a range, 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M (magenta, blue, green and red lines, respectively).

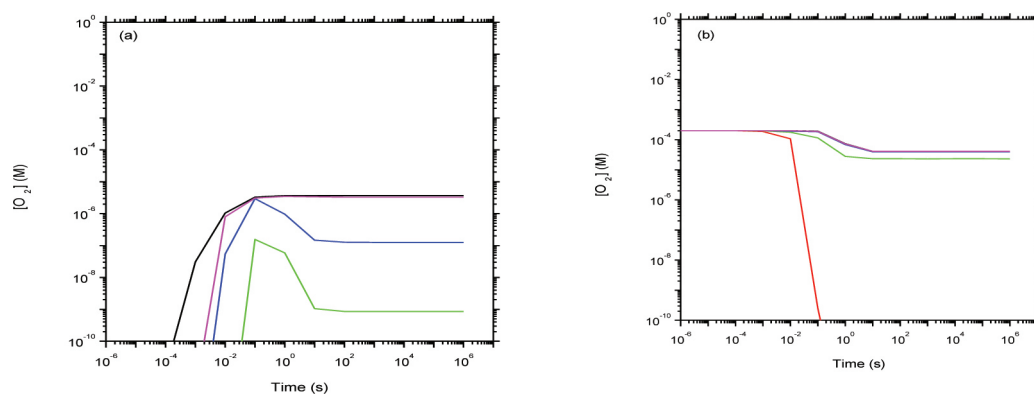


Figure 2: Time evolution of $[O_2]$ (in Molar) of pure water (black lines) and aqueous hydrazine solutions at 250 °C, calculated using our FACSIMILE in deaerated (a) and aerated (b) condition at the assumption of dose rate 10^4 Gy s^{-1} . and by varying the concentration of hydrazine added to our system under a range, 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M (magenta, blue, green and red lines, respectively).

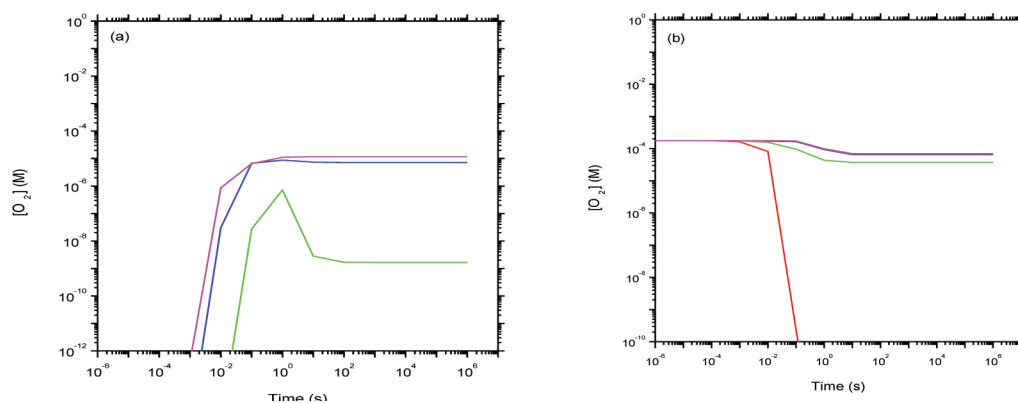


Figure 3: Time evolution of $[O_2]$ (in Molar) of pure water (black lines) and aqueous hydrazine solutions at 300 °C, calculated using our FACSIMILE in deaerated (a) and aerated (b) condition at the assumption of dose rate 10^4 Gy s^{-1} . and by varying the concentration of hydrazine added to our system under a range, 10^{-6} , 10^{-5} , 10^{-4} , and 10^{-3} M (magenta, blue, green and red lines, respectively).

whereas a slightly decrease of O_2 occurred due to the addition of 10^{-4} M hydrazine. For aerated conditions, similarly to the results at room temperature in Figure 1b, concentrations of O_2 falls down significantly at aqueous solution of 10^{-3} M hydrazine concentration.

For the case of increasing 225 centigrade temperature and above, concentrations of the O_2 reach steady state values more rapidly than those in room temperature. In other words, the higher the temperature the faster decreasing of O_2 since the reactions for O_2 consumption take faster proportionally to the temperature then O_2 production as in room temperature.

Unfortunately, regarding the water chemistry in hydrazine aqueous systems, there is however a complete lack of information on the radiolysis of water by fast neutron irradiation as the experimental data is not available in the literature to the best of our knowledge therefore we are not able to validate our results especially at high temperature.

The simulation results for room temperature, for deaerated condition, the varying concentration of added hydrazine in the range between 10^{-6} – 10^{-4} M has no effect in reaching the steady state concentration of O_2 and it is similar as in the pure water system and for 10^{-3} M hydrazine addition, a large produce of O_2 were obtained. In reverse, for deaerated condition, the concentration of hydrazine about 10^{-3} M can suppress the formation of O_2 significantly, while the addition of hydrazine in the range between 10^{-6} – 10^{-4} M is confirmed to be the same as in pure water system.

Overall, in all case, steady state concentrations of O_2 in the results of simulations for 250 and 300 °C are lower than those in room temperature both in the presence or absence of air. In deaerated condition, hydrazine addition can suppress the formation of O_2 proportionally to its concentration

4. Conclusion

In this work, FACSIMILE was used to calculate oxidator concentration, O_2 on coolant water radiolysis by fast neutrons irradiation at temperatures between 25 and 300 °C. The simulations also conducted in pure water and hydrazine aqueous solution both in the presence and absence of air. The time evolution of $[O_2]$ were obtained by taking into consideration the assumption of high dose rate conditions of fast neutron, a typical condition in reactor core (10^4 Gy s^{-1}).

The higher hydrazine concentrate, the lower O_2 . The highest concentration of hydrazine can suppress O_2 form until it becomes negligible. In aerated condition, hydrazine absent addition give the same result with 10^{-6} and 10^{-5} M of hydrazine where a slightly decrease of O_2 occurred due to the addition of 10^{-4} M hydrazine. However, experimental data are required to test more thoroughly our modeling calculations, and to specify the potential role of hydrazine to suppress of O_2 form.

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