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Boric Acid Radiolysis in Primary Coolant Water of PWR at Temperature of 250°C

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ARTICLE INFORMATION

ABSTRACT

BORIC ACID RADIOLYSIS IN PRIMARY COOLANT WATER OF PWR AT TEMPERATURE OF 250°C. The existence of oxygen in the primary coolant system of PWR could lead to corrosion, hence it is very important to suppress the oxygen concentration in the system. Therefore, study of the effect of boric acid addition into the primary coolant water system of PWR to suppress oxygen concentration resulted from gamma-ray radiation is essential to be performed. The aim of this research is to understand reaction mechanism at temperature of 250^0C and the effect of boric acid adding toward oxygen concentration in the PWR primary coolant water. Methodology used is simulation using Facsimile software. Input for the software namely radiolysis reaction mechanism for pure water, G value from radiolysis product, dose rate of 1 and 10^4 Gy/s, aeration and deaeration system, and specific reaction of boric acid with hydroxyl radical and hydrated electron at temperature 25^0C and 300^0C. The output are in the form of irradiation time vs oxygen concentration time series. The results show that the oxygen production increase significantly with the irradiation time and reach the saturated concentration at 10^7s. Based on the plot of oxygen's concentration at 10^7s vs boric acid, several results are as following: oxygen concentration significantly suppressed by boric acid addition and gives the exponential decreasement, the higher dose rate gives the higher concentration of oxygen, the aeration system gives no effect on suppressing oxygen concentration at boric acid addition up to 0.1M.

ABSTRAK

RADIOLISIS ASAM BORAT DI AIR PENDINGIN PRIMER PWR PADA TEMPERATUR 250°C. Adanya oksigen di dalam sistem pendingin primer PWR dapat menyebabkan korosi sehingga sangat penting untuk menekan konsentrasi oksigen dalam sistem tersebut**.** Oleh karena itu, **s**tudi pengaruh penambahan asam borat ke dalam air pendingin primer dari PWR untuk menekan konsentrasi oksigen yang dihasilkan akibat radiasi sinar-gamma penting untuk dilakukan. Tujuan penelitian adalah untuk memahami mekanisme reaksi hingga temperatur 250^0C dan pengaruh penambahan asam borat terhadap konsentrasi oksigen di dalam sistem pendingin primer PWR. Metodologi yang digunakan adalah simulasi menggunakan perangkat lunak Facsimile. Input yang digunakan adalah mekanisme reaksi radiolisis untuk air murni, nilai-G dari produk radiolisis, laju dosis 1 dan 10^4 Gy/*s*, sistem aerasi dan deaerasi, dan reaksi spesifik dari asam borat dengan radikal hidroksil dan electron terhidrasi, pada temperatur 25^oC dan 300^oC. Keluarannya berupa data runtun waktu iradiasi vs konsentrasi oksigen. Hasil simulasi menunjukkan bahwa produksi oksigen naik secara signifikan dengan lamanya waktu iradiasi dan mencapai kondisi tunak pada t=10^7*s*. Berbasis hasil plot antara konsentrasi oksigen pada t=10^7*s* vs konsentrasi asam borat, memberikan hasil sebagai berikut: konsentrasi oksigen ditekan secara signifikan oleh adanya asam borat dan memberikan penurunan secara eksponensial, pengaruh laju dosis menunjukkan bahwa semakin tinggi laju dosis maka oksigen yang dihasilkan akan semakin banyak, dan pada kondisi aerasi, penambahan asam borat hingga 0,1 M tidak memberikan efek yang berarti terhadap penekanan konsentrasi oksigen.
Kata kunci: radiolisis, asam borat, sinar gamma, facsimile, konsentrasi oksigen

1. INTRODUCTION

Boron, as boric acid, is being added in the primary water coolant system of Pressurized Water Reactor (PWR) as a fine neutron moderator [1–4]. In addition to that, boric acid has been used for moderating the coolant water in interim spent fuel storage at accident affected Fukushima units. The effect of boric acid on oxidator and reductor species, that have been generated by irradiation have not

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known yet, especially at high temperature up to 250°C. This is very important to understand the chemically condition, especially for the purpose on suppressing the corrosion process. The oxidator species are oxygen and hydrogen peroxide, and the reductor species are hydrogen gas.

The effect of boric acid addition in order to suppress the concentration of oxygen at room temperature by using Facsimile computer code has been done before[5]. The higher concentration of boric acid has been added up then the suppressed oxygen concentration will be much more. The linear relation between boric acid concentration and the degradation of oxygen in logarithm curve is well understood. However, the behavior at higher temperature of 250°C is not known yet.

The objective of this paper is to understand the effect of boric acid addition toward the oxygen under γ-rays irradiation up to temperature of 250°C. The methodology applied is simulation by using 'Facsimile' software[6-8]. Inputs are reactions mechanism of pure water radiolysis, G-values of radiolysis products, dose rate of 1 and 10^4 Gy/s, aeration and deaeration system, and specific reactions of boric acid with hydroxyl radical and hydrated electron, that are set for 25 and 250°C. Outputs are series of irradiation time vs concentration of oxygen.

2. METHODOLOGY

The simulation method has been reported elsewhere [5,9-14]. Radiolysis simulation is an analysis of simultaneous chemical reactions and the integration of time-dependent multivariable simultaneous differential equations. A computer code 'FACSIMILE' was used to integrate differential equations. As inputs the G-values, reaction set and rate constants are needed.

2.1. G-values

One of the important inputs at this simulation by using Facsimile software is G-values, that is defined as a number of radicals or molecules produced per 100 Ev energy absorbed. Set of radiolysis product as G-

values employed in this simulation is shown in Table 1.

2.2. Reactions Set

Set of reactions employed at this work, is based on Elliot's compilation [15] for pure water and listed in Table 2. In the simulation at room temperature, the reaction set is exactly the same as previous work [5,14]. Since the system is boric acid, therefore the reaction set of boric with probable radiolysis products is required. Two reactions of boric acid toward ·OH and $e_{aq}-$, were added to Elliot's reaction set (Table 2) [16]. Those rate constants at 25°C are well clarified but not for the higher temperature. Therefore, the rate constant of those reactions at 300°C was estimated by Arrhenius-type extrapolation using the activation energy of 70 kJ/mol.

Table 1. G-Values of Radiolysis Products Induced By γ-Rays Irradiation at 25 and 250°C.[9-16]

	γ-rays	
	25°C	250°C
e_{aq}^{-}	2.75	3.43
H	0.6	1.56
H$^+$	2.75	3.43
OH	2.81	5.74
H$_2$	0.44	0.64
H$_2$O$_2$	0.71	0.265
−H$_2$O	4.23	6.27

2.3. Dose Rate

A very high dose rate of radiation which is coming from γ-rays, fast neutrons and α-rays, is exposed by the core in PWR. Different type of PWR may initiate a different dose rates in the core, and dose rate distribution is really depend on the distance from the core. In this simulation, dose rate used is reported elsewhere, as 1 and 10^4 Gy s^{-1}, and only for γ-rays irradiation[1].

2.4. Water Chemistry Condition

Boric acid concentration was induced in the simulation up to 1 M. Literally the concentration range applied in the field is around 0.3 M, but in this study the input data applied up to 1 M. The objective is to understand the concentration effect based on

direct interaction between γ-rays irradiation and water. Therefore, no direct irradiation effect to the boric acid is considered. The initial concentration of oxygen which represents the aeration system is applied with the concentration of 2.5×10^{-4} M at 25°C[14].

3. RESULTS AND DISCUSSION

The simulation of radiolysis at 250°C was carried out. The validation of the sub routine was done and has been reported separately.[1,15]The results gave a good compromising with the previous work. Based on this, the further simulation of the effect at 250°C was done. The time variation of oxygen concentration is shown in Figure 1. It shows the effect of boric acid addition on oxygen production under γ-rays irradiation at 250°C in deaeration and aeration system, dose rate of 10^{4}Gy/s, and in the comparison with the at 25°C.

The profile at 25°C in deaeration system is shown in Figure 1.a. In Figure 1.b, it is clear that the oxygen is produced in deaerated pure water which is irradiated by using γ-rays at 250°C. The concentration depends on the irradiation time, get the optimum concentration in a certain irradiation time, and then become in a steady state condition. Compare with that in pure water profile, it shows that the existence of boric acid suppresses the oxygen concentration at its steady state condition. At the higher concentration of boric acid, the lower oxygen concentration is produced at its steady state condition. The effect of boric acid starts at different irradiation time, and seems faster at the higher concentration of boric acid.

Compare with that at Fig. 1.a., it is known that at higher temperature give the lower concentration of oxygen at its steady state condition. The effect of boric acid for both temperature clearly shows to suppress the oxygen suppressing, but it seems to be more effective at 250°C.

In the comparison of Fig.1.a. and c., for pure water under dose rate of 10^{4}Gy/s, it is clear that both systems give the same concentration of oxygen at its steady state condition. It can be understood that the presence of oxygen in aeration system does

not give any significant effect on the oxygen production. However, the effect of boric acid addition seems to be less productive in aeration system.
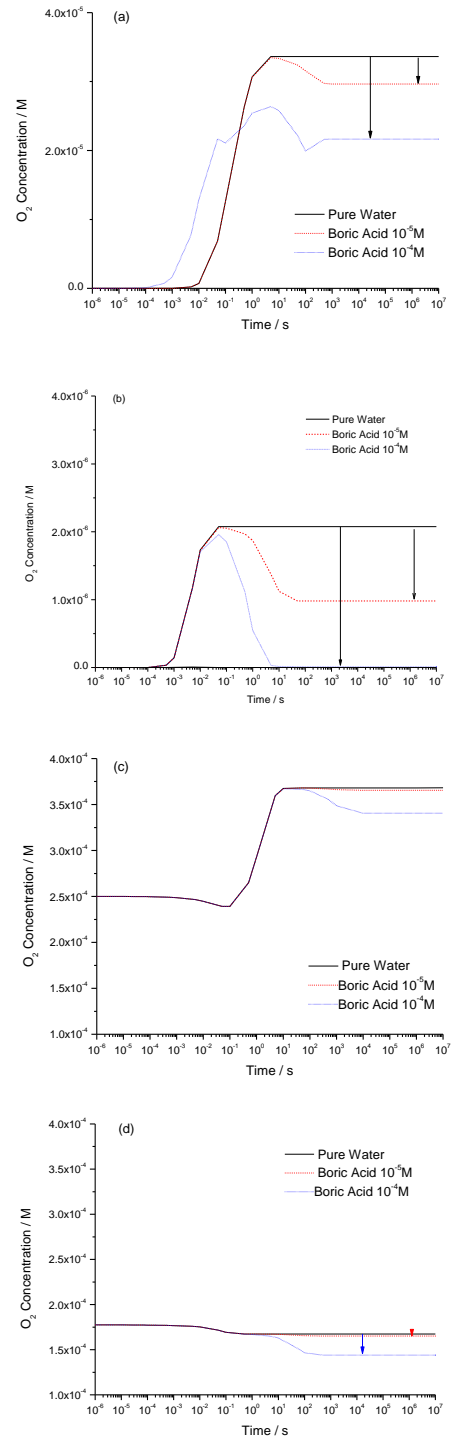

Figure 1. Time Variations of Oxygen Products in Various Water Chemistry Systems Under γ-Rays Irradiation (10^{4}Gy/S) At (A) 25°C, Deaeration System, (B) 250°C, Deaeration System, (C) 25°C, Aeration System and (d) 250°C, Aeration System.

By comparing Fig. 1c and d, it can be concluded that the initial oxygen concentration at 250°C is lower than at 25°C due to the density effect which is becoming approx. 0.8 at 250°C. Therefore, the steady state concentration of oxygen is becoming lower than that at 25°C. The effect of the boric acid existence, give a similar effect with that at 25°C.
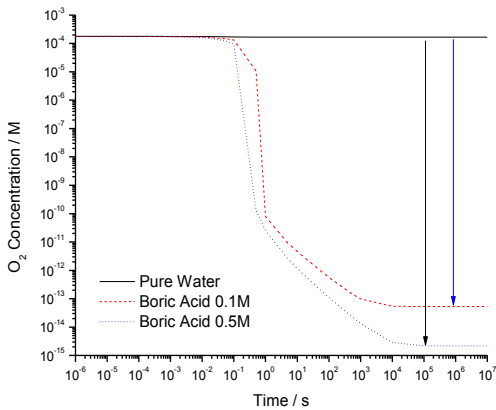

Figure 2. Time Variations of Oxygen Products in Aeration System with The Higher Boric Acid Addition, Under γ–Rays Irradiation (10^4Gy/S) at 250°C.

In the Figure 2, it shows that in the addition of boric acid, 0.1M, the oxygen production in aerated system is suppressed drastically, becoming in the range of 10^{-14}M, compare with that at Fig.1.d. that still in the range concentration of 10^{-4}M, at its steady state condition.

The steady state concentration of oxygen at various conditions, in pure water, under γ–rays irradiation at 250°C is listed at Table 3.

Table 3. The Steady State Concentration of Oxygen at Various Conditions, in Pure Water, Under γ–Rays Irradiation at 250°C.

Dose rate (Gy/s)	System	Steady state oxygen concentration/M
10^4	Aeration	3.68×10^{-4}
	Deaeration	3.36×10^{-5}
1	Aeration	2.07×10^{-4}
	Deaeration	1.26×10^{-7}

It is clear that at 250°C, the dose rate effect is insignificant for aeration system, but 2 magnitudes different for deaeration system.

The boric acid concentration variations of oxygen products at its steady state concentration (at 10^7s), in aeration system, under γ–rays irradiation (10^4Gy/s), at 250°C, is shown in Figure 3.

The boric acid at low concentration of under 0.2M, is very effective to suppress oxygen production, and become less significant for further concentration. While for boric acid concentration bigger than 0.2M, the effect in aeration and deaeration system is negligible. The dose rate difference gives eligible effect clearly, which is at lower dose rate give the lower oxygen concentration. It means that the boric acid concentration is excess, therefore the scavenging capacity is very high toward oxygen at both deaeration and aeration system.
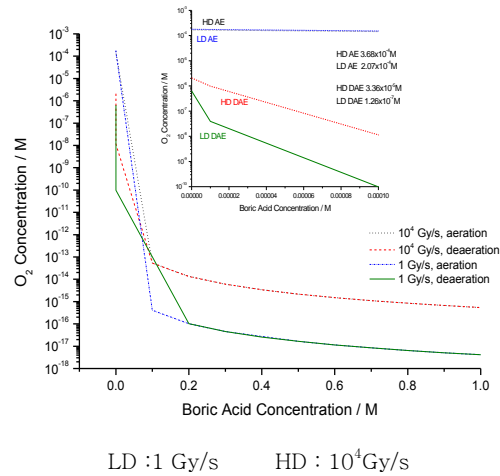

LD :1 Gy/s   HD : 10^4Gy/s

Figure 3. Boric Acid Concentration Variations of Oxygen Products at Its Steady State Concentration (at 10^7s), in Aeration System, Under γ–Rays Irradiation (10^4Gy/s), at 250°C.

4. CONCLUSION

Boric acid can suppress the presence of oxygen on primary water of PWR. The phenomenon is exponential decreasement. The presence of oxygen nearly depleted at boric acid addition up to 0.2M. Further than that, the decreasement becomes less. It is understood that boric acid reacts mainly with hydroxyl radical than that with hydrated electron.

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Table 2. Reaction set in pure water system is based on Elliot's compilation.[15]

No	Reaction	$k/dm^3mol^{-1}s^{-1\bullet1}$	
		25°C	250°C
1.	$e_{aq}- + e_{aq}- + 2H_2O = H_2 + 2OH^-$	$7.26x10^9$	$5.92 x10^9$
2.	$e_{aq}- + H + H_2O = H_2 + OH^-$	$2.76x10^{10}$	$4.97 x10^{11}$
3.	$e_{aq}- + OH = OH^-$	$3.50x10^{10}$	$3.73 x10^{11}$
4.	$e_{aq}- + H_2O_2 = OH + OH^-$	$1.40x10^{10}$	$3.85 x10^{11}$
5.	$e_{aq}- + O_2 = O_2^-$	$2.30 x10^{10}$	$2.18 x10^{11}$
6.	$e_{aq}- + O_2^- + 2H_2O = H_2O_2 + 2OH^-$	$1.30 x10^{10}$	$1.61 x10^{11}$
7.	$e_{aq}- + HO_2 = HO_2^-$	$1.28 x10^{10}$	$1.61 x10^{11}$
8.	$H + H = H_2$	$5.14 x10^9$	$1.04 x10^{11}$
9.	$H + OH = H_2O$	$1.10 x10^{10}$	$6.34 x10^{10}$
10.	$H + H_2O_2 = H_2O + OH$	$3.60 x10^7$	$2.15 x10^9$
11.	$H + O_2 = HO_2$	$1.30 x10^{10}$	$6.06 x10^{10}$
12.	$H + HO_2 = H_2O_2$	$1.13 x10^{10}$	$2.14x10^{11}$
13.	$H + O_2^- = HO_2^-$	$1.03 x10^{10}$	$2.14x10^{11}$
14.	$OH + OH = H_2O_2$	$4.80 x10^9$	$9.87 x10^9$
15.	$OH + H_2 = H_2O + H$	$4.15 x10^7$	$7.8 x10^8$
16.	$OH + H_2O_2 = HO_2 + H_2O$	$2.87 x10^7$	$4.23 x10^8$
17.	$OH + HO_2 = O_2 + H_2O$	$8.80 x10^9$	$3.20 x10^{10}$
18.	$OH + O_2^- = OH^- + O_2$	$1.10 x10^{10}$	$8.98 x10^{10}$
19.	$HO_2 + HO_2 = H_2O_2 + O_2$	$8.40 x10^5$	$4.10 x10^7$
20.	$HO_2 + O_2^- + H_2O = H_2O_2 + O_2 + OH^-$	$1.00 x10^8$	$1.02 x10^7$
21.	$O_2^- + O_2^- + H_2O = H_2O_2 + O_2 + OH^-$	0.3	$2.28 x10^4$
22.	$H_2O = H^+ + OH^-$	$2.12 x10^{-5}$	$6.52 x10^{-2}$
23.	$H^+ + OH^- = H_2O$	$1.18 x10^{11}$	$1.13 x10^{12}$
24.	$H_2O_2 = H^+ + HO_2^-$	$6.49 x10^{-2}$	$2.52 x10^1$
25.	$H^+ + HO_2^- = H_2O_2$	$4.52 x10^{10}$	$5.69 x10^{11}$
26.	$H_2O_2 + OH^- = HO_2^- + H_2O$	$1.18 x10^{10}$	$1.36 x10^{11}$
27.	$HO_2^- + H_2O = H_2O_2 + OH^-$	$9.97 x10^5$	$1.76 x10^8$
28.	$H = H^+ + e_{aq}-$	$3.70 x10^0$	$1.65 x10^5$
29.	$H^+ + e_{aq}- = H$	$2.02 x10^{10}$	$7.16 x10^{11}$
30.	$e_{aq}- + H_2O = H + OH^-$	$1.23 x10^1$	$8.03 x10^9$
31.	$H + OH^- = e_{aq}- + H_2O$	$1.86 x10^7$	$2.01 x10^3$
32.	$OH = H^+ + O^-$	$6.49 x10^{-2}$	$2.52 x10^1$
33.	$H^+ + O^- = OH$	$4.52 x10^{10}$	$5.69 x10^{11}$
34.	$OH + OH^- = O^- + H_2O$	$1.33 x10^{10}$	$1.36 x10^{11}$
35.	$O^- + H_2O = OH + OH^-$	$1.27 x10^6$	$1.76 x10^8$
36.	$HO_2 = H^+ + O_2^-$	$8.19 x10^5$	$7.32 x10^8$
37.	$H^+ + O_2^- = HO_2$	$5.02 x10^{10}$	$5.69 x10^{11}$
38.	$HO_2 + OH^- = O_2^- + H_2O$	$9.78 x10^{-2}$	$2.87 x10^4$
39.	$O_2^- + H_2O = HO_2 + OH^-$	$1.18 x10^{10}$	$1.36 x10^{11}$
40.	$O^- + H_2 = H + OH^-$	$1.17 x10^8$	$1.55 x10^9$
41.	$O^- + H_2O_2 = HO_2 + OH^-$	$5.53 x10^8$	$8.18 x10^{10}$
42.	$OH + HO_2^- = O_2^- + H_2O$	$8.29 x10^9$	$8.18 x10^{10}$
43.	$O^- + OH = HO_2^-$	$7.60 x10^9$	$3.38 x10^{10}$
44.	$e_{aq}- + HO_2^- = O^- + OH^-$	$3.50 x10^9$	$6.90 x10^{10}$
45.	$e_{aq}- + O^- + H_2O = OH^- + OH^-$	$2.31 x10^{10}$	$9.10 x10^{10}$
46.	$O^- + O_2 = O_3^-$	$3.47 x10^9$	$3.26 x10^{10}$
47.	$O_3^- = O^- + O_2$	$1.90 x10^3$	$1.99 x10^7$
48.	$H + H_2O = OH + H_2$	0	$2.10 x10^3$
49.	$H_2O_2 = OH + OH$	0	$2.14 x10^{-1}$
50.	$OH + H_3BO_3 = H_2O + H_2BO_3$	$5 x10^4$	$8.46 x10^5$
51.	$e_{aq}- + H_3BO_3 = H + H_2BO_3^-$	$3 x10^4$	$5.06 x10^5$