A Water Radiolysis Code for the Irradiation Loop System*

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Abstract

In order to evaluate the water chemistry in the irradiation field during IASCC irradiation test, a water radiolysis code for the irradiation loop system was developed. In the water radiolysis code, a multiple node model was introduced since the irradiation loop system has a wide range temperature distribution as well as dose distribution. To investigate applicability of the developed water radiolysis code, water chemistry at the water sampling point of the irradiation loop system was measured and compared with analytical results under several water chemistry conditions. Further, water chemistry distribution in the in-pile region as well as in the out-pile region was calculated by the developed water radiolysis code.

Key words: Water Radiolysis Code, IASCC, Water Chemistry, Irradiation Research, JMTR

1. Introduction

Irradiation assisted stress corrosion cracking (IASCC) is recognized as an important degradation issue of the core-internal material for aged Boiling Water Reactors (BWRs). Therefore, the irradiation loop system has been developed and installed in the Japan Materials Testing Reactor (JMTR) to perform the IASCC irradiation test. In the IASCC irradiation test, water chemistry at the irradiation field is one of the most important key parameters because it affects initiation and propagation of cracks. It is, hence, important to know the water chemistry conditions which simulate BWR's beforehand in view point of advanced irradiation test. On the other hand, it is well known that the measurement of the water chemistry at the irradiation field is quite difficult. Therefore the water radiolysis code for irradiation loop system was developed based on the WRAC code⁽¹⁾. In the water radiolysis code, direct generation of radiolytic species due to radiation energy deposition in the water, secondary generation and disappearance are introduced. Typicality of the water radiolysis analysis on the irradiation loop system is treatment of wide range temperature distribution, i.e. R.T. to about 561K. To treat such a wide range temperature distribution, multiple nodes model is introduced in this code.

In order to confirm the applicability of the developed water radiolysis code, water chemistry in the irradiation loop was calculated. Further, experiments to measure the water chemistry of irradiation loop system were performed. Obtained experimental data were compared with the calculated result. This paper describes the modeling of the water radiolysis code for irradiation loop system and the applicability of the developed water radiolysis code.

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2. Overview of the irradiation loop system

A schematic diagram of the irradiation loop system is shown in Fig.1. The irradiation loop system consists of the water control unit (WCU) and capsules. Major specifications of the WCU are described in Table 1. The WCU supplies high temperature and high pressure water in order to simulate BWR's condition. In the water conditioning tank, O_2 concentration and H_2 concentration are controlled by bubbling of mixed gas of oxygen-helium, hydrogen-helium or pure helium. Two of the three main pumps usually operate to prevent loss of flow from the safety point of view. To reduce fluctuation of flow rate, the main pump of three plungers is employed and a surge tank of forty liters is installed at outlet of the main pumps. At the downstream of the regenerative heat exchanger, feeding water line is divided into five paths to the capsules. Headers and coolers of the high capacity are employed to maintain the temperature of feeding water because 100% of flow rate should be cooled for purification and then heated again for temperature control of specimens. Instrumentation for on-line monitoring is provided and batch sampling can also be done for water chemistry analysis. In the water chemistry measurement, O_2 concentration, H_2 concentration and conductivity are measured by on-line monitoring whereas H_2O_2 and impurities are measured by batch sampling. In the irradiation loop

Table 1 Major specifications of the WCU.

Capacity	5 capsules Temperature 593K (Max.) Pressure 10MPa (Max.) Flow Rate 0.2m ³ /h/capsule
Temp. of specimens	561K ^{+14K} _{-26K} for all specimens
Water chemistry Conductivity Impurities	< 10μS/m SO ₄ ²⁻ < 5ppm Fe, Cr < 10ppb
Dissolved Oxygen	controllable between 10 - 200ppb
Dissolved Hydrogen	controllable below 1ppm

Fig. 1 A schematic diagram of the irradiation loop system.

system, water chemistry at the outlet of the water conditioning tank, inlet as well as outlet of in-pile region can be measured.

Schematically drawn cross section of a capsule^{(2),(3)} is shown in Fig.2. A capsule contains several types of irradiation specimens such as compact tension (CT) specimens, uniaxial constant load (UCL) specimens and so on. Temperature of test specimens is controlled by the saturation temperature of feeding water. By controlling the water pressure, temperature of all specimens in a capsule is controlled within the range from 535K to 575K during irradiation experiments.

Fig. 2 A schematic diagram of a capsule.

3. Development of Water Radiolysis Code

In order to evaluate the water chemistry in the irradiation loop system, the water radiolysis code (WRAC-JM) was developed based on the WRAC code⁽¹⁾. In the WRAC-JM code, direct generation of radiolytic species due to radiation energy deposition in the water, secondary generation and disappearance caused by their interaction, interaction with surfaces are introduced. Further, a multiple node model has been introduced since the irradiation loop system has a wide range temperature distribution as well as the dose distribution. The basic equations are shown in Eq.(1),

$$\frac{\partial C_i^k}{\partial t} = g_i^\gamma Q^{gk} + g_i^n Q^{nk} + \sum k_{mn}^i C_m^k C_n^k - C_i^k \sum k_{is} C_s^k + \sum k_{mn}^{wi} C_m^k C_n^k - C_i^k \sum k_{is}^{wk} C_s^k + C_i^{k-1} \frac{G_{in}^k}{V^k} - C_i^k \frac{G_{out}^k}{V^k} \quad (1)$$

where C_i : concentration (mol/l), g : G-value (1/100MeV), γ : γ ray, n : neutron, Q : absorption dose rate (Gy/s), V : volume (m^3), k : reaction rate constant (l/mol/s), k^w : reaction rate constant with surface (l/mol/s), G_{in} and G_{out} : flow velocity at inlet and outlet of the node, respectively. The first and second terms of right side are direct generation of radiolytic species by γ ray and neutron. In this code, eight kinds of radiolysis products; e^- , H , H^+ , OH , OH^- , H_2 , H_2O_2 , HO_2 are considered. G-values⁽⁴⁾ of radiolytic species at 558K employed in this study are shown in Table 2. The third and fourth terms are secondary generation and disappearance by their interaction. The fifth and sixth terms are generation and disappearance with surface. The seventh and eighth terms are connection with adjacent nodes. Schematic diagram of node connection is shown in Fig.3. As shown in this figure, initial condition of the adjacent node is given by following simple formula;

$$C_i^{j,in} = C_i^{j-1,out} \quad (2)$$

where $C_i^{j,in}$: initial concentration at node j (mol/l), $C_i^{j-1,out}$: output concentration at node $j-1$ (mol/l). It should be mentioned at the node connection that temperature difference at each node causes density change, therefore concentration is compensated based on the temperature at node as follows;

$$C_i^{j,in} = \frac{\rho_j}{\rho_{j-1}} C_i^{j-1,out} \quad (3)$$

where ρ_j : density of water at node j (kg/m^3), ρ_{j-1} : density of water at node $j-1$ (kg/m^3).

Fig. 3 Node connection with adjacent nodes.

Table 2 High temperature G-values⁽⁴⁾.

Species	Gamma rays	Neutrons
e ⁻	3.50	0.60
H	0.90	0.50
H ⁺	3.50	0.60
H ₂	0.60	1.50
H ₂ O ₂	0.55	1.14
HO ₂	0.00	0.04
OH	4.50	1.70
OH ⁻	0.00	0.00

One of the typicality on calculation of the irradiation loop system is wide range temperature distribution from R.T. to about 573K. To treat such a wide range temperature distribution, reaction rate constants were given by extrapolation from the 561K values assuming Arrhenius equation and activation energy as follows;

$$k(T) = k(T_0) \exp \left\{ \left(\frac{1}{T_0} - \frac{1}{T_i} \right) \frac{Q}{R} \right\} \quad (4)$$

where T_0 : standard temperature (K), T_i : temperature at a node (K), Q : activation energy (J/mol), k : reaction rate constant (l/mol/s), R : gas constant (8.31J/mol/K). Reaction rate constants and activation energy⁽⁴⁾⁻⁽⁶⁾ employed in this study is shown in Table 3.

Main components in the irradiation loop system were modeled into several regions. Fig.4 shows the calculation model for the irradiation loop system. Normally main components

Table 3 Rate constants and activation energies⁽⁴⁾⁻⁽⁶⁾.

Reaction	Rate constant at 558K (dm ³ /mol/s)		Activation Energy (J/mol)	
	FORWARD	REVERSE	FORWARD	REVERSE
$H^+ + OH^- \rightarrow H_2O$	1.90×10^{12}		1.26×10^4	
$H_2O_2 \rightarrow 1/2 O_2 + H_2O$	$1.40 \times 10^{-2} *$		6.00×10^4	
$e^- + H_2O \rightarrow H + OH^-$	2.90×10^2		1.26×10^4	
$e^- + H^+ \rightarrow H$	2.60×10^{11}		1.26×10^4	
$e^- + OH \rightarrow OH^-$	2.90×10^{11}		1.26×10^4	
$e^- + H_2O_2 \rightarrow OH + OH^-$	2.40×10^{11}		1.26×10^4	
$H + H \rightarrow H_2$	9.00×10^{10}		1.26×10^4	
$e^- + HO_2 \rightarrow HO_2^-$	3.00×10^{11}		1.26×10^4	
$e^- + O_2 \rightarrow O_2^-$	2.60×10^{11}		1.26×10^4	
$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$	1.75×10^6		1.26×10^4	
$2OH \rightarrow H_2O_2$	2.50×10^{10}		8.40×10^3	
$OH^- + H \rightarrow e^- + H_2O$	7.00×10^8		1.26×10^4	
$e^- + H + H_2O \rightarrow OH^- + H_2$	4.82×10^9		1.26×10^4	
$e^- + HO_2^- + H_2O \rightarrow OH + 2OH^-$	5.35×10^8		1.26×10^4	
$H + OH \rightarrow H_2O$	2.30×10^{11}		1.26×10^4	
$OH + H_2 \rightarrow H + H_2O$	1.40×10^9		1.93×10^4	
$H + O_2 \rightarrow HO_2$	1.50×10^{11}		1.26×10^4	
$H + HO_2 \rightarrow H_2O_2$	3.00×10^{11}		1.26×10^4	
$H + O_2^- \rightarrow HO_2^-$	3.00×10^{11}		1.26×10^4	
$e^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$	3.57×10^9		1.26×10^4	
$H + H_2O_2 \rightarrow OH + H_2O$	2.00×10^9		1.89×10^4	
$OH + H_2O_2 \rightarrow H_2O + HO_2$	4.20×10^8		1.43×10^4	
$OH + HO_2 \rightarrow H_2O + O_2$	1.00×10^{11}		1.26×10^4	
$2HO_2 \rightarrow H_2O_2 + O_2$	5.00×10^7		1.89×10^4	
$HO_2 \rightarrow O_2^- + H^+$	$3.90 \times 10^5 *$	7.70×10^{11}	1.26×10^4	1.26×10^4
$HO_2 + O_2^- \rightarrow O_2 + HO_2^-$	5.00×10^8		1.89×10^4	
$O_2^- + OH \rightarrow OH^- + O_2$	2.90×10^{11}		1.26×10^4	
$2O_2^- + 2H_2O \rightarrow O_2 + H_2O_2 + 2OH^-$	1.27×10^5		1.89×10^4	
$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	1.00×10^{10}	2.14×10^5	1.26×10^4	1.26×10^4
$* H_2O_2 \rightarrow 2OH$	$2.3 \times 10^{-4} **$		6.00×10^4	

★ : Surface reaction

*:s⁻¹

** :ms⁻¹

such as heat exchangers and pipes have temperature distribution. Therefore, such main components were divided to several nodes to introduce the temperature effect. The capsule was also modeled into several nodes in connection with the structure and fluence distribution. Modeling of the in-pile region is shown in Fig.5. In the capsule, large amount of test specimens are installed, then input information such as surface area, volume were evaluated precisely.

One through type calculation is performed for the irradiation loop system. According to the calculation model shown in Fig.4, contents of O₂, H₂, H₂O₂ and other radicals is calculated along with the water flow. In the calculation, consumption of oxidizing species due to oxidation of metallic surface is not considered because enough prefilming treatment by high temperature as well as highly oxygen concentrated water had been performed before the loop operation.

Fig. 4 Calculation model for the irradiation loop system.

Fig. 5 Calculation model for the in-pile region.

4. Discussions

4.1 Water chemistry measurement

In order to evaluate water chemistry variables in the irradiation loop system, O_2 concentration, H_2 concentration and H_2O_2 concentration are measured by online monitoring or batch sampling. In viewpoint of corrosion phenomenon, it is well known that O_2 and H_2O_2 are important parameters because they increase the electrochemical corrosion potential (ECP) of stainless steel, whereas hydrogen decrease the ECP. At the outlet of the water conditioning tank, the water chemistry is monitored not only for evaluation but also to control O_2 concentration, H_2 concentration in supply water. In addition, outlet water as well as inlet water of the in-pile region is measured by selecting sampling selection valves as shown in Fig. 1. In the irradiation loop system, O_2 concentration and H_2 concentration are

Fig. 6 Apparatus for determination of H_2O_2 .

measured by polarographic type sensors (DKK-TOA Co.Ltd.), and these are installed in the WCU for online monitoring. On the other hand, measurement method for H_2O_2 concentration is quite different from others. For understanding the concentration of H_2O_2 in the irradiation loop, high detection level of sub-ppb is required. One of the most promising methods for H_2O_2 detection is the chemical photoluminescence, using luminol as a chemical phosphor. In order to detect H_2O_2 by the chemical photoluminescence method, the flow injection type H_2O_2 detection method⁽⁷⁾ was employed in the irradiation loop system. A schematic diagram of this method is shown in Fig.6. The carrier water is supplied continuously into a mixing joint. The mixed reagent which is consisted of luminol, Co^{2+} , and buffer solution and carrier water are fed into the mixing joint with the same flow rate. 20 μl of sample water are fed into the mixing joint by rotating the injection valve. H_2O_2 in the sample water reacts with the luminol on passing into the flow cell. Then the luminous intensity is measured by the chemiluminescence analyzer CLA-2100 (Tohoku Electronic Industrial Co.,Ltd.).

4.2 Evaluation

In this study, distributions of O_2 , H_2 and H_2O_2 in the capsule as well as in the WCU were calculated using the WRAC-JM code. The absorption dose rate distribution of neutron as well as γ -ray for in-pile region is shown in Fig.7. Values of the absorption dose rate are described in Table 4. Major input parameters such as temperature, surface area/volume (S/V) ratio and residence time for each node in WCU and in-pile region are described in Table 5. In this table, parameters are indicated as range (min-max) for each component. It is clear from this table that S/V ratio at the capsule is quite large compared to that of other components. In order to confirm the applicability of water radiolysis code, several cases were calculated. Calculation cases are shown in Table 6. In this table, values mean the initial condition at the water conditioning tank and three of four cases simulate NWC condition, the rest simulates HWC conditions.

Fig.8 shows comparison between measured and calculated result at the sampling point of the irradiation loop system. In this figure, horizontal-axis shows the measured values and vertical-axis shows the calculated values, (a), (b), (c) and (d) show concentration of H_2O_2 , H_2 , O_2 and effective oxygen concentration ($[\text{O}_2]_{\text{eff}}$), respectively. ($[\text{O}_2]_{\text{eff}}$ is defined as $[\text{O}_2]_{\text{eff}} = [\text{O}_2] + 1/2[\text{H}_2\text{O}_2]$ ⁽⁸⁾) From this figure, it can be said that O_2 , H_2 concentration and $[\text{O}_2]_{\text{eff}}$ relatively agree well with measured data. On the other hand, measured H_2O_2 concentration was quite small since H_2O_2 decomposes by heat during passing through the high temperature area at the sampling line. From the comparison between measured and calculated result on H_2O_2 concentration, good enough coincidence cannot be observed. One of the reasons for this is considered that temperature measurement point around the

Table 4 Absorption dose rate at in-pile region.

Position	Absorption dose rate (Gy/s)	
	Neutron	γ -ray
node 28	142	307
node 27	372	603
node 26	487	823
node 25	574	988
node 24	818	1040
node 23	926	1020
node 22	766	962
node 21	613	952

Table 5 Major input parameters.

Components	Node	Temperature (K)	S/V ratio (1/m)	Residence Time (sec)	Flow velocity (m/sec)
Water conditioning tank	1	310	-	-	-
Pipe-1	2	310	142	4.6	0.48
Main pump	3 - 5	310	94 – 160	17.3 – 26.4	0.21 – 0.60
Pipe-2	6 - 7	310	206	6.0	0.84 – 1.00
Heat exchanger	8 - 11	346 – 452	104 – 308	26.4 – 32.8	0.22 – 0.43
Pipe-3	12 – 13	452	206	4.4 – 9.2	0.26 – 0.94
Heater	14 - 17	469 – 521	46	105.0 – 113.8	0.0035 – 0.0038
Pipe-4	18 - 20	521 – 523	160 – 666	1.9 – 13.4	0.18 – 3.06
Capsule	21 - 28	524 – 556	105 – 1891	0.3 – 8.3	0.056 – 0.213
Pipe-5	29 - 30	541	280 – 667	5.8 – 13.2	0.56 – 3.18
Pipe-6	31 - 33	522	104 – 280	2.0 – 5.4	0.075 – 1.04
Heat exchanger	34 – 37	419 – 488	104 – 217	2.8 – 19.3	0.25 – 1.05
Pipe-7	38	385	206	4.3	0.88
Cooler	39 – 42	327 – 366	104 – 217	3.1 – 25.8	0.22 – 0.95
Pipe-8	43 – 49	308	13 – 206	1.9 – 317.4	0.006 – 1.0
Sampling pipe-1	50 - 60	541 – 476	114 – 920	0.2 – 51.8	0.008 – 0.56
Cooler	61 – 64	472 – 306	261	40.0 – 46.0	0.041 – 0.036
Sampling pipe-2	65 - 66	306	273 - 513	24.5 – 100.6	0.14 – 0.28

Table 6 Calculation cases.

Condition		[O ₂] (ppb)	[H ₂] (ppb)	[H ₂ O ₂] (ppb)
NWC	Case-1	170	2	9
	Case-2	50	3	16
	Case-3	10	4	10
HWC	Case-4	0	60	14

Fig. 7 Absorption dose rate distribution at in-pile region.

sampling line in the irradiation loop system is not enough to evaluate the decomposition behavior of H_2O_2 . Therefore precise temperature evaluation of sampling line is required for more precise H_2O_2 evaluation.

Fig.9 shows the water chemistry distributions obtained by the WRAC-JM. In Fig.9, (a), (b), (c) and (d) show concentration of H_2O_2 , H_2 , O_2 and $[\text{O}_2]_{\text{eff}}$, respectively. Each concentration depends on location in the irradiation loop system. Typically, the extreme change in concentration is observed at the irradiation field due to water radiolysis by neutron or gamma-ray. In view point of IASCC irradiation research, the water chemistry at the irradiation field is of much interest. In case of NWC, H_2O_2 concentration increased up to 250ppb in case-1, O_2 as well as H_2O_2 decreases by decreasing O_2 injection. In case of HWC, increase of $[\text{O}_2]_{\text{eff}}$ was governed by H_2O_2 but it suppressed at quite low level lower than 15ppb.

Employing the water radiolysis code, precise water chemistry at the in-pile region as well as out-pile region, relation of the initial condition of supply water and water chemistry in the in-pile region can be evaluated. In other words, important information for IASCC irradiation tests can be obtained by this water radiolysis code. However, it should be mentioned that calculated results at the irradiation field is not confirmed by the direct measurement. Hence, based on the corrosive environmental standpoint, validation by ECP measurement is expected.

Fig. 8 Comparison between measured and calculated results.

Fig. 9 Water chemistry distribution obtained by the WRAC-JM.

5. Conclusions

In this study, the water radiolysis code for irradiation loop system was developed. Calculation results obtained by the developed water radiolysis code were compared with experimental data. The comparison results on O_2 , H_2 concentration and $[O_2]_{eff}$ showed relatively good agreement between calculation results and experimental data. Further, water chemistry at the irradiation field which gives important information for IASCC irradiation research can be obtained from the water radiolysis code.

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