Predicted water chemistry for current and advanced light water reactors

YEH Tsung-Kuang[1], and WANG Mei-Ya[2]

1. Department of Engineering and System Science, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013, R.O.C. (tkyeh@mx.nthu.edu.tw)
2. Nuclear Science and Technology Development Center, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013, R.O.C. (meywang@mx.nthu.edu.tw)

Abstract: Intergranular stress corrosion cracking (IGSCC) on stainless steel and nickel-base alloy components has been a major material degradation issue for decades for all light water reactors (LWRs) around the world. To ensure operation safety, an optimization on the coolant chemistry in the primary coolant circuit of a nuclear reactor is essential no matter what type or generation the reactor belongs to. In light of the safety demand and the lack of essential water chemistry information in a LWR, the only feasible approach to accomplish the foregoing task of understanding water chemistry state is to conduct a series of theoretical analyses. In this study, a radiolysis model was therefore developed for analyzing the concentrations of electro active radiolysis products in the coolant. The simulation would produce predicted results pertinent to the water chemistry variation and the corrosion behavior of structure materials in the primary coolant system of a LWR.

Keyword: light water reactor; water chemistry; radiolysis

1 Introduction

In light water reactors (LWRs), water is circulated through the reactor core, as a moderator and a coolant. In a pressurized water reactors (PWR), the reactor coolant system consists of a primary coolant circuit and a secondary coolant circuit. The coolants in these two circuits bear distinctly different compositions. In a boiling water reactor (BWR), there is only one primary coolant circuit. An advanced boiling water reactor (ABWR) represents an evolutionary route for the BWR family, with numerous changes and improvements to previous BWR designs. Supercritical water reactors (SCWRs) are similar to LWRs but operate at relatively higher pressure and temperature over the supercritical point of 22.1 MPa and 374 ^{o}C. Pure water of oxidizing nature is used as the coolant. It is the water chemistry of the coolant that dominates the structural integrity of an LWR. From the perspective of a comprehensive and proactive design, an appropriate control over the water chemistry of the coolant in an LWR is essential. For mitigating IGSCC in LWRs, hydrogen is added into the reactor coolant for maintaining a reducing environment in an LWR [1]. The only feasible approach to accomplish the task of understanding the water chemistry profile along the primary coolant circuit of an LWR is to conduct a series of theoretical analyses. Radiolysis models were therefore developed for analyzing the concentrations of all possible radiolysis products in the reactor coolant and the corrosion behavior of structure materials in the primary coolant system of an LWR may be produced.

2 Radiolysis and water chemistry

2.1 Radiation chemistry

Neutrons, gamma rays, fission products, alpha and beta particles of various radiation energies generated in the reactor core and absorbed in coolant is mainly attributed to fast neutrons and gamma rays. Absorption of energy in the coolant results in water radiolysis, which occurs in all light water reactors. Tracks and spurs are formed along the moving path of the particles or gamma rays during the water radiolysis process. Various radiolytic species are produced inside them. In BWRs and ABWRs, after the irradiation of neutrons and gamma photons on the reactor water, a number of radiolytic products are generated. In PWRs, additional irradiation should be taken into account due to the reaction of $^{10}B(n,\alpha)^{7}Li$. In order to quantify the radiolytic yield during the water radiolysis process, the term G value is created. The G value is the number of atoms, ions, radicals, or molecules formed or decomposed after 100 eV energy of the radiation source is absorbed by the water. G

values can be influenced by system temperature and are therefore different in LWRs.

All species present in the reactor water could interact with one another (*i.e.* undergo chemical reactions). At the steady state, an equilibrium will be reached and the concentration of each species will remain unchanged. The chemical reactions taking place in the reactor water are complicated. The number of reactions involved usually exceed 30 in the BWR coolant and 50 in a PWR. Each reaction has its own reaction rate constant, and the magnitude of this rate constant must be derived experimentally. The reaction rate constant varies with the system temperature, and Arrhenius law is usually adopted as an alternative.

2.2 Modeling structure

The DEMACE computer code consists of a radiolysis model for calculating chemical species concentration, and a mixed potential model for calculating the electrochemical corrosion potential (ECP).[2] The water radiolysis model, which calculates the concentrations of radiolysis products from the decomposition of water due to neutron and gamma irradiation, forms the base of this algorithm. The radiolysis model takes into account the chemical reactions coupled to fluid convention to calculate the concentrations of the species in the primary coolant circuit (PCC) of a nuclear reactor. Once the species concentrations have been determined in the PCC, the ECP is calculated using a mixed potential model (MPM).

3 Modeled reactors

3.1 Boiling water reactor

For simplicity in modeling, the entire PCC of a BWR was divided into 12 regions in the DEMACE computer model, as shown in Fig. 1. The DEMACE computer code consists of a radiolysis model for calculating chemical species concentration, a mixed potential model for calculating ECP, and a coupled environment fracture model for calculating the crack growth rate. According to EPRI water chemistry guidelines, the well-recognized ECP of -0.23 V_{SHE} is considered a conservative corrosion potential (E_{crit}) for the majority of structural alloys in typical BWR environments. Based upon this criterion, a component is considered protected from IGSCC and the

hydrogen water chemistry (HWC) technique is deemed effective if the predicted ECP is below the E_{crit}.

1. Core Channel   2. Core Bypass   3. Upper Plenum
4. Stand Pipe   5. Separator Sideway   6. Mixing Plenum
7. Upper Downcomer   8. Lower Downcomer   9. Recirculation System
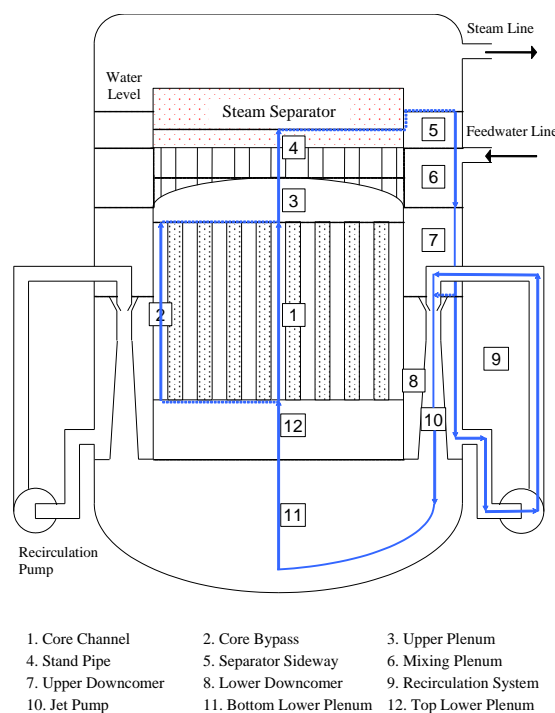10. Jet Pump   11. Bottom Lower Plenum   12. Top Lower Plenum

Fig. 1. Conceptual configuration of a typical BWR primary coolant circuit.

3.1.1 Power uprate

Power up rates have become a common practice for the power utilities owning LWRs to meet the increasing electricity demand under the restrictions of constructing new nuclear power plants. Among the three types of power uprate, measurement uncertainty ($< 2\%$), stretch power uprate (2 to 7%), and extended power uprate (7 to 20%, currently approved maximum percentage), there is no common selection for general nuclear power plants and a thorough evaluation is always required for every single LWR. When a reactor's power is uprated, changes in power density (*i.e.* neutron and gamma photon dose rates) and coolant flow velocity in the reactor core would lead to concentration variations of the major redox species. Accordingly, the required feedwater hydrogen concentrations ($[H_2]_{FW}$s) at different power levels for the HWC technology to take effect on IGSCC mitigation may thus be different.

Reactor X is a BWR-6 type reactor with a rated thermal power of 2894 MW, and its commercial operation started in December of 1981. It is currently operating under HWC with a 1.0 parts per million

(ppm) $[H_2]_{FW}$. Numerical simulations for Reactor X were carried out for $[H_2]_{FW}$ ranging from 0.0 to 2.0 ppm and for power levels ranging from 100% to 120%. Figure 2 shows variations in ECP as a function of $[H_2]_{FW}$ and power level at the bottom lower plenum outlet location.[3] A particular uprate percentage, however, would be expected to induce a relatively more oxidizing environment and hence led to a poorer HWC efficiency that was commonly seen at most of the evaluated locations of Reactor X with a 108% or 115% power level. On the other hand, the HWC efficiency would be slightly improved at the bottom lower plenum outlet at certain higher power levels of 107%, 114% and 120%. Finally, it is important to note that the uniquely oxidizing environment at the uprated power level of 108% or 115% was applicable to Reactor X only.
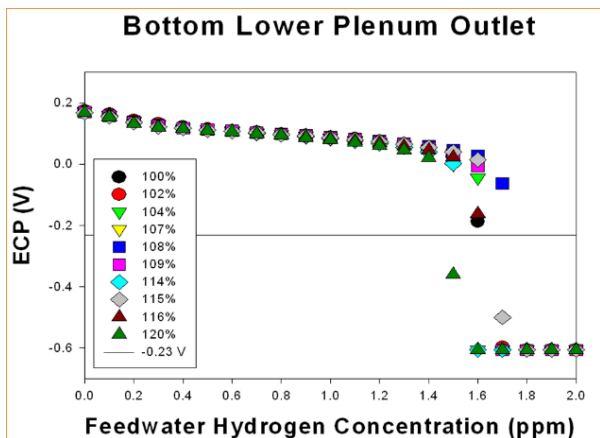

Fig. 2. Variations in ECP as a function of $[H_2]_{FW}$ at the bottom lower plenum outlet location of Reactor X with operating power levels ranging from 100% to 120% of the rated power.

3.1.2 Power coastdown

Current LWRs produce electric energy at their rated power level until the reactivity-limited burnup is reached. When all control rods are fully withdrawn and core flow is at or near the rated value to generate maximum power in an LWR near the end of its fuel cycle, a coastdown operation (*i.e.* gradually reduced power) may commence. For the domestic LWRs in Taiwan, a typical coastdown duration may last from a week to a month with a terminal operating power level at 90% to less than 100% of the rated value. The operating power would decrease one percent in about every two days. In a similar manner, a BWR may undergo a power coastdown operation near the end of a fuel cycle when the fuel in the core is sufficiently depleted earlier than scheduled and the rated power

can no longer be maintained. Upon a power coastdown, the power density and coolant flow velocity in the reactor core would accordingly change, followed by water chemistry variations due to reduced radiolysis of water and extended coolant residence times in the near-core regions.

Figure 3 shows variations in ECP as a function of $[H_2]_{FW}$ and power level at the recirculation system outlet of Reactor X.[4] The ECP monotonically increased with decreasing power level at this location, and the required $[H_2]_{FW}$ were 0.6, 0.7, and 0.8 ppm at the 100%, 95%, and 90% power levels, respectively. A lower operating power would increase the demand on the feedwater H_2 level at the recirculation system outlet. Summarizing the predicted ECP results at these four locations, we noted that no significant ECP differences due to power coastdown were observed when the $[H_2]_{FW}$ was either much less or greater than the critical concentration at which the ECP markedly decreased to below the E_{crit}. Furthermore, the impact of a power coastdown on the HWC efficiency would vary from plant to plant. An individual analysis on the impact of power coastdown on the corrosion mitigation effectiveness of HWC in a BWR is necessary.
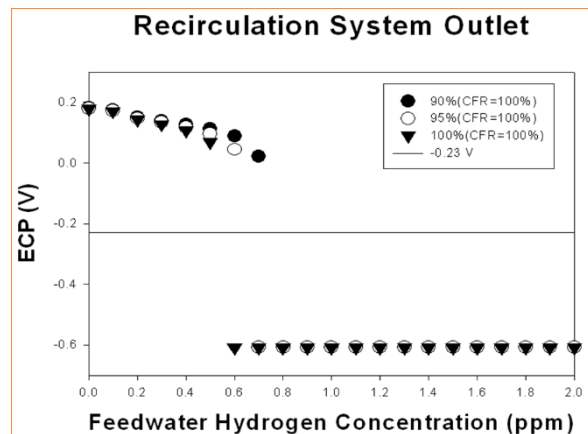

Fig. 3. Variations in ECP as a function of $[H_2]_{FW}$ at the recirculation system outlet location of Reactor X with operating power levels ranging from 90% to 100% of the rated power.

3.1.3 Impact of core flow rate

For a BWR operating under normal condition, the power density is not likely to change to a great extent in a fuel cycle, but the core flow rate (CFR) of the coolant usually does not remain constant throughout the entire cycle. During a typical fuel cycle of a BWR,

control rod pattern exchanges are periodically (40 to 60 days in general) adopted to maintain the designated reactivity in the reactor core. Changes in the CFR of a BWR would lead to concentration variations of the major redox species due to varied coolant residence times in the reactor core. Accordingly, the required $[H_2]_{FWS}$ at different CFRs for the HWC technology to take effect on IGSCC mitigation (*i.e.* to reduce the ECP to below -0.23 V_{SHE}) may thus be different.

Reactor Y is a BWR/4 type reactor with a rated thermal power of 1775 MW, and its commercial operation started in December of 1978. Numerical simulations were carried out for $[H_2]_{FW}$ ranging from 0.0 to 2.0 parts per million (ppm) and for CFR ranging from 80.6% to 100% in Reactor Y under rated power operation. Figure 4 shows variations in ECP as a function of $[H_2]_{FW}$ and CFR at the recirculation system outlet of Reactor Y. [5] The ECP decreased to below the E_{crit} at 0.6 ppm $[H_2]_{FW}$ at rated CFR but it became lower than the E_{crit} at 0.3 ppm $[H_2]_{FW}$ at 80.6% CFR. A lower CFR tended to lower the required concentration of H_2 in the feedwater at the recirculation system outlet. The impact of CFR on the water chemistry in the PCC of a BWR may vary from region to region. In addition, it is anticipated that a BWR with a different power density and different physical dimensions may respond to the changes in CFR in a unique manner, and an independent analysis is therefore necessary.

3.1.4 Impact of power startup

Most BWRs adopted moderate HWC (HWC-M) or low HWC combined with the noble metal to mitigate IGSCC during normal power operation. It is important to note that the hydrogen injection system could be used only during normal plant operation since hydrogen is usually injected into the feedwater. Therefore, the reactor coolant usually contains high levels of dissolved oxygen due to intrusion of atmospheric air during a cold shutdown, could remain relatively oxidizing under startup operations. As a matter of fact, some laboratory data have already indicated that under normal water chemistry (NWC) conditions the rates of IGSCC at intermediate temperatures during reactor startup and shutdown processes

were actually higher than those at operating temperatures. Several plants have implemented design changes to begin injecting hydrogen into the feedwater at low power (>5%) during startup to suppress IGSCC during these periods. A trial HWC during startup was demonstrated to evaluate the suppression of SCC initiation at some commercial plants.

Numerical simulation for predicting the water chemistry variation in Reactor Y was carried out for $[H_2]_{FW}$ ranging from 0.0 to 2.0 ppm condition and for the power levels from 3.8% to 11.3% observed during a typical startup operation in this study. Figure 5 shows variations in ECP as a function of $[H_2]_{FW}$ and power level at the upper plenum outlet location.[6] The required $[H_2]_{FW}$ to reduce the ECP below the E_{crit} at 3.8% rated power was 0.4 ppm, but HWC could become effective at 0.5 ppm $[H_2]_{FW}$ at power level of 5.2% at the upper plenum outlet. As a minor amount of steam started to generate in the reactor core at even higher power levels, the required $[H_2]_{FW}$ was shifted to 1.7, 1.0 and 0.9 ppm at power levels of 8.4%, 10.8% and 11.3%, respectively. One important phenomenon to note was that the ECP at 6.7% power level never went below the E_{crit} even though the $[H_2]_{FW}$ was high as 2 ppm. Summarizing the predicted ECP results, we found that significant variations in ECP could occur before and after the generation of steam in the core during a startup operation of Reactor Y. It is important to note that the predicted water chemistry during a startup operation is applicable to Reactor Y only.
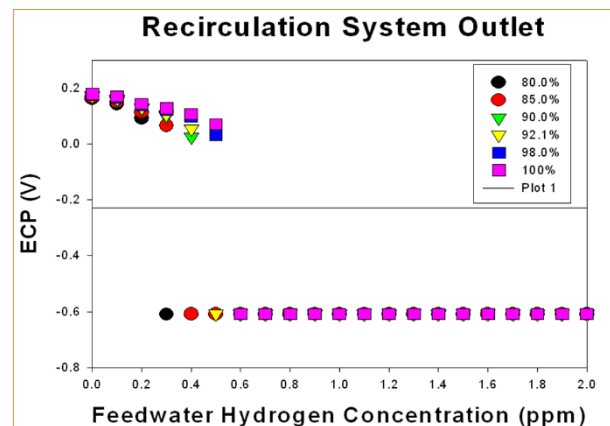

Fig. 4. Variations in ECP as a function of $[H_2]_{FW}$ at the recirculation system outlet location of Reactor Y with core flow rates ranging from 80.6% to 100% of the rated value.
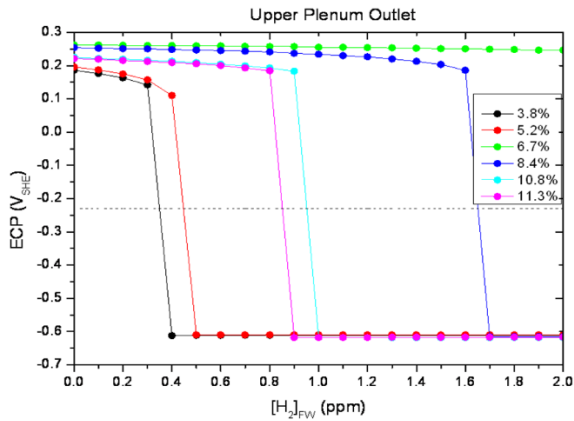
Fig. 5. Variations in ECP as a function of $[H_2]_{FW}$ at the upper plenum outlet location of Reactor Y during a startup operation.

3.2 Pressurized water reactor

In light of the safety demand and the lack of essential water chemistry information in a PWR, the only feasible approach to accomplish the foregoing task of understanding water chemistry state is to conduct a series of theoretical analyses. A radiolysis model was therefore developed for analyzing the concentrations of electro active radiolysis products in the coolant. The simulation would produce predicted results pertinent to the water chemistry variation and the corrosion behavior of structure materials in the primary coolant system of a commercial PWR.

Reactor Z is a three-loop Westinghouse PWR type reactor with a rated thermal power of 2775 MW, and its commercial operation started in July of 1984. For simplicity in modeling, the entire PCC of a PWR was divided into 9 regions in the DEMACE computer model, as shown in Fig. 6. Numerical simulations for predicting variations in the O_2, H_2, and H_2O_2 concentrations along the PCC of Reactor Z operating at rated power under 5, 30 and 70 c.c./kg injecting hydrogen concentration ($[H_2]_{inj}$), shown in Fig. 7.[7] More intense radiolysis effects on the reactor coolant were observed according to the predicted results on chemical species concentrations. The concentrations of the two oxidizing species (H_2O_2 and O_2) could become extremely high at locations inside the core. The concentrations of the two oxidizing species (H_2O_2 and O_2) decreased rapidly in the downcomer region. A higher injecting hydrogen significantly decreased the concentrations of the oxidizing agents along the PCC. It is important to note that the

predicted water chemistry at rated power is applicable to Reactor Z only.
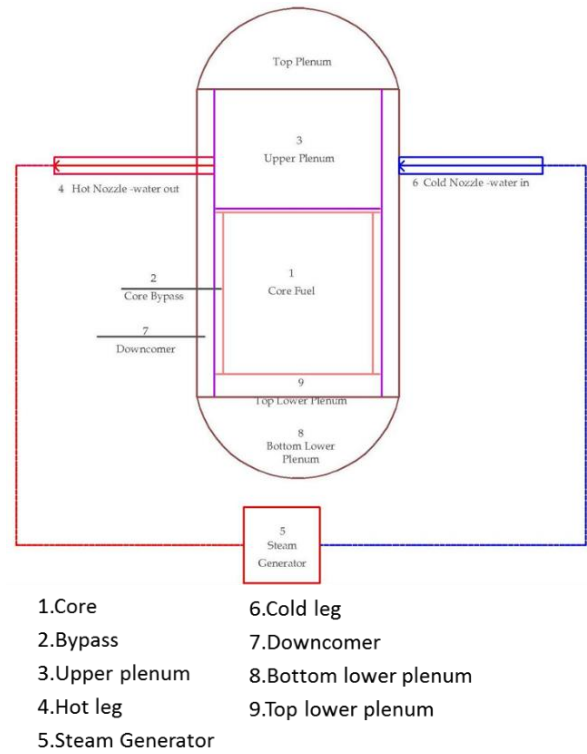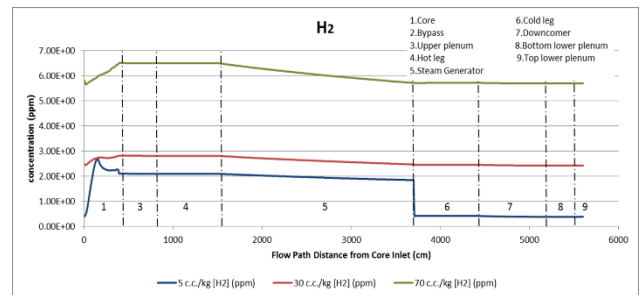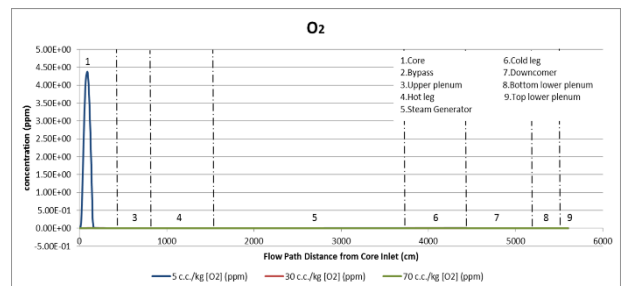

1.Core   6.Cold leg
2.Bypass   7.Downcomer
3.Upper plenum   8.Bottom lower plenum
4.Hot leg   9.Top lower plenum
5.Steam Generator

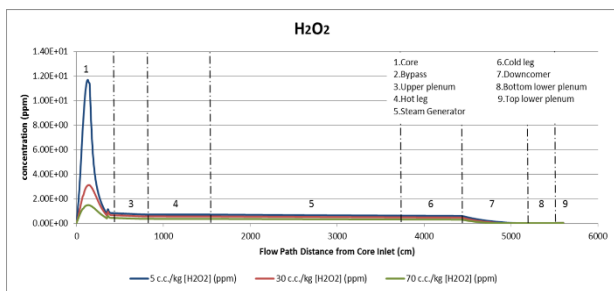Fig. 6. Conceptual configuration of a typical PWR primary coolant circuit.

(a) $[H_2]$

(b) $[O_2]$

(c) [H$_2$O$_2$]

Fig. 7. Variations in the species concentrations as a function of [H$_2$]$_{inj}$ along the PCC of Reactor Z at rated power.

3.3 Advanced boiling water reactor

For further improvements on thermal efficiency and operation safety, reactor internal pumps, instead of conventional recirculation systems, are adopted in an ABWR. With the novel design of internal circulation, the travelling path and pattern of the recirculated liquid coolant in an ABWR is actually different from that of the coolant in a conventional BWR. To ensure operation safety, optimization on the coolant chemistry in the primary coolant circuit of a nuclear reactor is essential no matter what type or generation the reactor belongs to. For a better understanding toward the water chemistry in an ABWR and for a safer operation of this ABWR, we conducted a proactive, thorough water chemistry analysis prior to the completion of this reactor. A well-developed computer code was used in the current study to investigate the effectiveness of hydrogen water chemistry on the redox species concentrations and ECP behavior of components in the primary coolant circuit of an ABWR.

An ABWR with a rated thermal power of 3926 MW and a coolant flow rate of 14502 kg/s was selected as the modeling target. For simplicity in modeling, the entire PCC of an ABWR was divided into 10 regions in the DEMACE computer model, as shown in Fig. 8. In this study, the water chemistry and ECP modeling was then carried out for the entire PCC of the targeting reactor with [H$_2$]$_{FW}$s ranging from 0.0 to 2.0 ppm. Figure 9 shows variations in ECP as a function of [H$_2$]$_{FW}$ at the five selected locations of the targeting ABWR.[8] At the upper plenum outlet of this ABWR, the ECP never went below the E$_{crit}$ even though the [H$_2$]$_{FW}$ was as high as 2.0 ppm at rated power operation. Similar situation occurred at the top

downcomer (Top DC) region, but the ECP would be lower than that at the upper plenum outlet. The ECP response was effectively reduced at a 0.4 ppm [H$_2$]$_{FW}$ at the outlets of the downcomer, the reactor internal pump (RIP) System, and the bottom lower plenum of this ABWR. As the [H$_2$]$_{FW}$ increased, the steady decrease of ECP in the downcomer region simply reflected a significant recombination of O$_2$ and H$_2$. The required [H$_2$]$_{FW}$s at these locations after the coolant entered the downcomer region will be smaller than those at the locations inside and near the core. An individual analysis on the corrosion mitigation effectiveness of HWC in an ABWR is necessary.
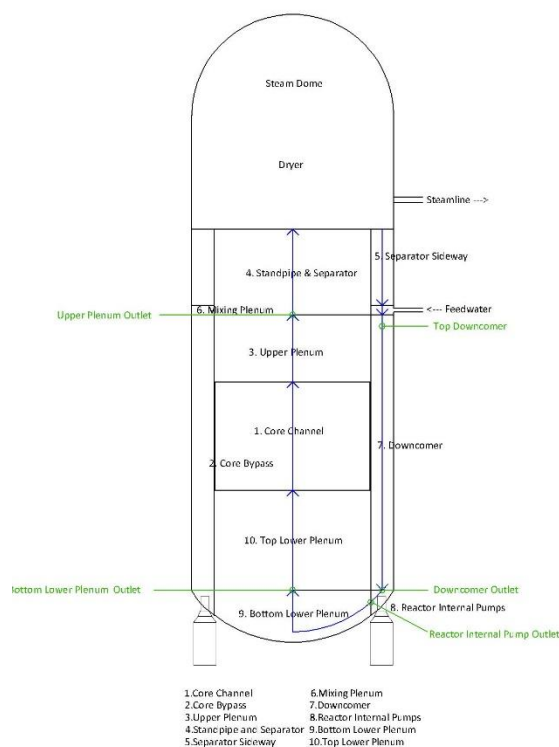

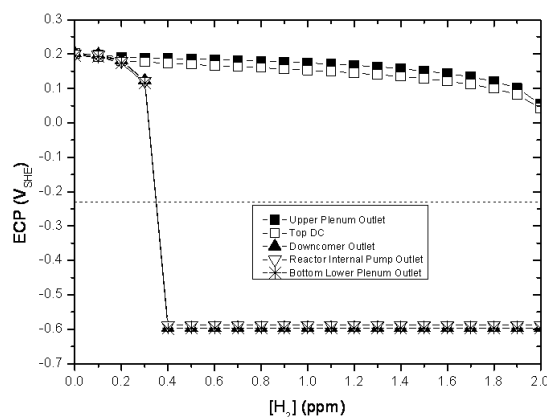Fig. 8. Conceptual configuration of a typical ABWR primary coolant circuit.

Fig. 9. Variations in ECP as a function of [H$_2$]$_{FW}$ at five selected locations of targeting ABWR at the rated power.

3.4 Supercritical water reactor

One of the Generation IV reactors adopts supercritical light water as the reactor coolant. While current in-service LWRs have an average thermal efficiency of 33%, the thermal efficiency of a SCWR could be more than 44%. For BWRs, the coolants are oxidizing due to the presence of hydrogen peroxide (H_2O_2) and oxygen (O_2), which are in turn generated by water radiolysis and the decomposition of H_2O_2, respectively. The oxidizing coolant ultimately leads to the degradation of structural materials, mainly stress corrosion cracking. Unlike the limited solubility in LWR coolants, oxygen is completely soluble in supercritical water. Furthermore, the average power density of the studied SCWR was 69.4 kW/L, relatively higher than that (~50kW/L) of a commercial BWR. Due to the higher power density of an SCWR, the degree of water radiolysis would become more intense, and higher concentrations of the oxidizing species can be expected. Accordingly, the greater oxidizing power and a relatively high coolant temperature should cause worse degradation phenomena in the structural and core components of an SCWR than in a BWR. To ensure proper design of the structural components and suitable selections of the materials to meet the requirements of operation safety, it is essential to begin to define the water chemistry in the PCC. In this study, a U.S. designed SCWR with a rated thermal power of 3575 MW and a coolant flow rate of 1843 kg/s was selected as the modeling target.

Numerical simulations for predicting variations in the O_2, H_2, and H_2O_2 concentrations along the PCC of the targeting SCWR operating at rated power were carried out. For simplicity in modeling, the critical portion of the PCC, which is located inside the pressure vessel of an SCWR, was divided into 13 regions in the DEMACE model, as shown in Fig. 10.[9] Simulation results on variations in the concentrations of major redox species under NWC and HWC conditions along the PCC of this SCWR are presented. The concentrations of radiolysis species calculated in this study were for steady state, not for transient state. It was the balance between the accumulation of these species produced by radiolysis and the consumption of them by radiolytic recombination that led to the convergence of our

calculation and determined the steady-state concentrations of major redox species. The predicted species concentrations under NWC and HWC conditions along the PCC of the targeting SCWR are shown in Fig. 11. Summarizing the predicted variations in the concentrations of major redox species under NWC along the PCC, we found that significant variations in [H_2], [O_2] and [H_2O_2] occurred along the PCC of this SCWR. High levels of oxidizing species could exist in the regions in and near the core, such as the core channel, the middle water rod, and the upper plenum regions. The phase change of the coolant in the core channel region due to the temperature increase led to more intense radiolysis and a coolant density change of nearly an order of magnitude, and that resulted in a sharp increase in the concentrations of all major redox species, especially oxidizing species. Therefore, the structural materials in an SCWR may be exposed to an environment not only with a much higher temperature but also even more oxidizing than that in a BWR. In view of the outcome of the recombination reactions between H_2 and the oxidizing species in certain regions, an addition of extra H_2 into the reactor coolant could be a feasible approach to reducing the concentrations of H_2O_2 and O_2 and render the coolant a reducing environment. Finally, it is important to note that the predicted results obtained in this study are only suitable for the conceptual SCWR design we selected, and water chemistry in SCWRs with different specifications should be evaluated separately.

1. Core Channel   6. Upper Downcomer   11. Lower Water Rod
2. Core Bypass   7. Lower Downcomer   12. Lower Plenum
3. Upper Plenum   8. Upper Head   13. Fission Gas Plenum
4. Hot Nozzle   9. Upper Water Rod
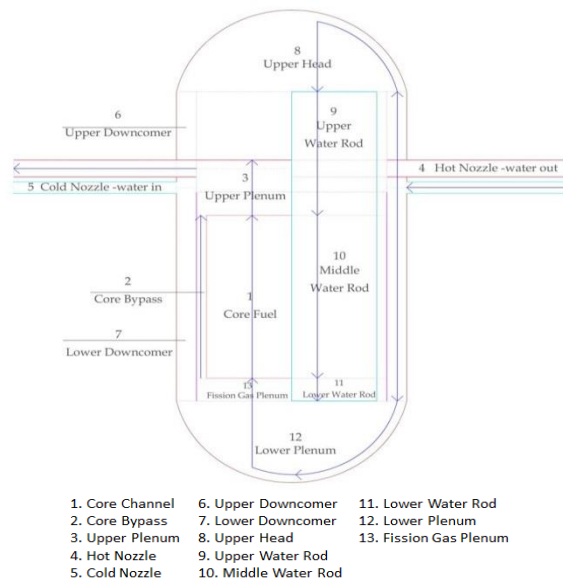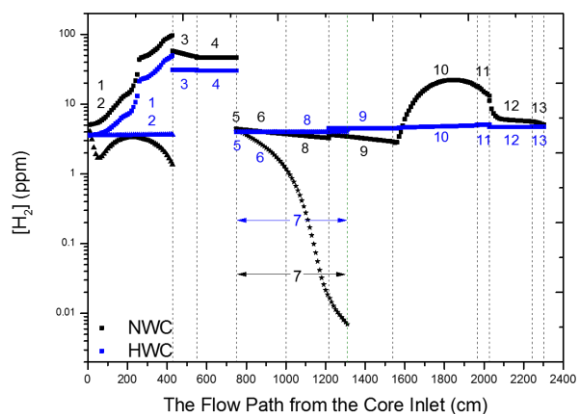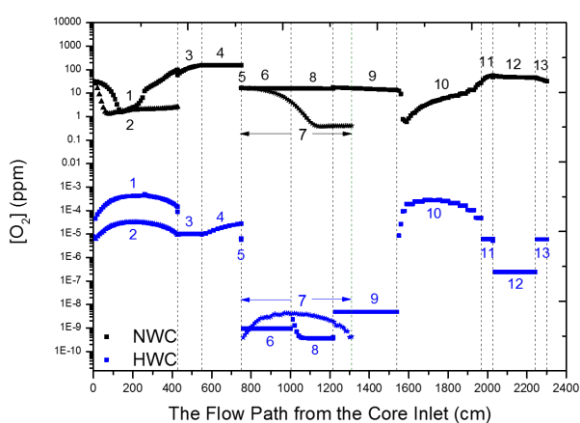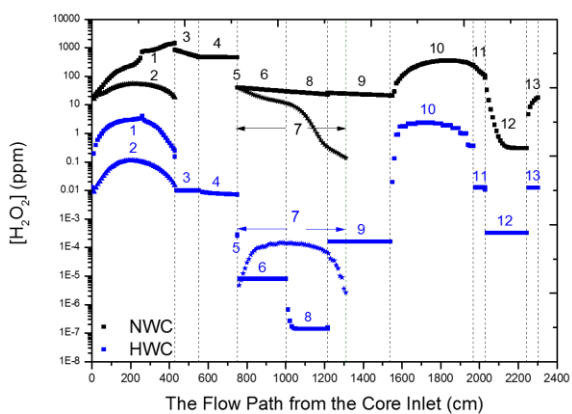5. Cold Nozzle   10. Middle Water Rod

Fig. 10. Conceptual configuration of the primary coolant circuit in an SCWR.

(a) [H$_2$]

(b) [O$_2$]

(c) [H$_2$O$_2$]

Fig. 11. Variations in the species concentrations under NWC and HWC conditions along the PCC of targeting SCWR at rated power.

4 Conclusions

Corrosion and the resultant degradation in components of LWRs, old or new, is impossible to stop in the future. As far as the reactor design is concerned, water chemistry improvement will play an extremely important role on maintaining structural integrity in a new LWR. Appropriate tools such as

numerical modeling must be adopted to help better understand the water chemistry in the primary coolant circuit of an LWR since every LWR is unique.

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