



Original Article

Radiochemical behavior of nitrogen species in high temperature water

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ABSTRACT

The water radiolysis in-core at light water reactors (LWRs) produces various radicals with other ionic species/molecules and radioactive nitrogen species in the reactor coolant. Nitrogen species can exist in many different chemical forms and recirculate in water and steam, and consequently contribute to what extent the environmental safety at nuclear power plants. Therefore, a clear understanding of formation kinetics and chemical behaviors of nitrogen species under irradiation is crucial for better insight into the characteristics of major radioactive species released to the main steam or relevant coolant systems and eventually development of advanced processes/methodologies to enhance the environmental safety at nuclear power plants. This paper thus focuses on basic principles on electrochemical interaction kinetics of radiolytic molecules and various nitrogen species in high temperature water, fundamental approaches for calculating thermodynamic values to predict their stability and domain in LWRs, and the effect of nitrogen species on crevice chemistry/corrosion and intergranular stress corrosion cracking (IGSCC) susceptibility of structure materials in high temperature water.

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1. Introduction

Nuclear energy is recognized as a critical part of decarbonized energy systems in emitting the least greenhouse gas and managing associated climate changes. Since major components of commercial nuclear reactors were manufactured with metallic alloys, both academic and industrial efforts have been devoted to selecting and evaluating the proper structure materials and their performance in nuclear environments [1–8]. The intense energetic neutron fluxes and γ -radiation at nuclear reactor in-core create a harsh environment which produces displacement damage of materials and radiolytic decomposition of the coolant water. Materials in a reactor thus experience the most extreme conditions that can have a major impact on the performance, safety, and reliability of nuclear power plants (NPPs).

Over the last several decades, scientific approaches, through research and development programs, led to better understanding of degradation mechanisms of major structure components in high temperature water both with and without radiation, and considerable progresses have been made on the modeling, prevention,

and monitoring technologies for enhancing the safety and performance of nuclear reactors. Substantially a number of materials challenges have been successfully resolved, but continuous improvements on the operational reliability, economics, and safety of reactors are still pursued.

Nevertheless, IGSCC is still the most concern as the predominant degradation mode of structural materials in LWRs and a very complex phenomenon affected by several variations including microstructures of materials, stress conditions, and environments. Mechanistic understanding of radiation damage processes in LWR core-component alloys is thus a critical underpinning issue for the effective operation of existing commercial reactors [4–7]. The aqueous environment chemistry and component stress/strain conditions strongly influence the IGSCC susceptibility of components. IGSCC failures occur in structural components exposed to a significant flux of neutron radiation in the reactor coolant environment, known as irradiation-assisted stress corrosion cracking (IASCC). The existence of surface conditions (e.g., cold work, strains at welding zone, irradiation hardening) at in-core components elevates the complicate mechanism and kinetics for crack initiation/growth associated with the radiolysis of coolant.

The primary products by the radiation-induced water decomposition are mainly in chemical and charge balances, and their input rates strongly depend on the dose rate. The interaction of

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high energy radiation, such as γ -radiation, with aqueous environments produces a host transient radicals, ions, and stable molecular species, such as *H , *OH , e_{aq}^- , H_3O^+ , OH^- , H_2 , O_2 , H_2O_2 , etc. Among them, e_{aq}^- and *H are reducing species, whereas *OH is a powerful oxidizing radical, and the productions of primary radical species strongly vary with the pH of aqueous environments. Since active radiolysis species interact with other products and alter the chemical reactions, corrosion kinetics of reactor structural components are also affected. The water chemistry condition in the reactor coolant is thus an important contributor for reliable plant operation, safety integrity, component lifetime, environmental impact, etc. at NPPs.

Ammonia is currently added as a source of hydrogen by radiolytic decomposition in-core at Russian Water-Water Energy Reactor (VVER) plants [9]. Hence, under aqueous ammonia environments, interaction of nitrogen species with various oxidizing radicals (e.g., O_2 , *OH) may affect the integrity of structural components. It has been reported that most of nitrogen chemicals were found in the cationic form, mostly NH_4^+ and the anion fraction was found to contain two major species, NO_3^- and NO_2^- , in both reactor coolant and steam condensate [10]. One can then postulate that the presence of such nitrogen species in LWR coolant may alter the water chemistry condition, in particular, at some localized areas (crevice, cracks, etc.) that results in changes on the corrosion kinetics of structural materials under irradiation.

Therefore, it is very important to understand the radiochemical behavior and stability of ammonia and other nitrogen species in reactor coolant and they need to be seriously addressed. Nonetheless, the clear mechanism on chemical interactions of nitrogen species still remains a challenge with reference to creation of corrosive environment. Thus, the purpose of this paper is mainly to describe thermodynamics and chemical behaviors of various radicals and nitrogen species under irradiation for getting a better comprehension of environmental interaction with structural materials in LWR water.

2. Electrochemistry of hydrogen, oxygen, and hydrogen peroxide in high temperature water

Electrochemical reaction at the metal/water interface is important for understanding electron transfer reactions that contribute to the thermodynamic stability of materials in the system. Most of metal-water systems have been well established and documented in the form of potential (E)-pH diagram (known as a Pourbaix diagram) [11–13], which is characterized by three basic domains of immunity, corrosion, and passivity and clearly depicts the thermodynamic stable regions of metal and metal oxides in water at temperatures.

The E-pH diagram presents only the equilibria at various pHs and potentials among metal, metal ions, metal oxides, and hydroxides for systems, but it gives no information about the kinetics of the corrosion process. Nevertheless, the E-pH diagram is extensively used to rationalize electrochemical corrosion processes for metals in aqueous solution. Both cathodic and anodic processes take place at the metal surface and the overall corrosion process is thermodynamically possible under the conditions stated only if the equilibrium reaction potential for the cathodic process is more positive than the equilibrium potential for the anodic reaction.

Considering the LWR coolant chemistry containing the most stable molecules, e.g., O_2 , H_2 and H_2O_2 , the E-pH diagram is traced for the equilibrium reactions taking place in reactor water and consequently the E-pH relationship of water stable domain corresponds to the equilibrium potential of predominant reactions (A) for H_2 oxidation, (B) for O_2 reduction, and (C) for H_2O_2 reduction as

[14,15];



Then, the equilibrium potentials for the above redox reactions can be calculated by the following Nernst equation:

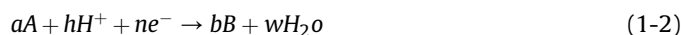
$$E = E^0 - \frac{RT}{nF} \ln \frac{(ox)}{(red)} \quad (1-1)$$

where E is the equilibrium potential, E^0 is the standard electrode potential, R is the gas constant, T is the absolute temperature, n is the number of electrons, F is the Faraday constant, and (ox) and (red) are the concentrations of oxidized (H_2 oxidation) and reduced species (O_2 or/and H_2O_2 reduction), respectively.

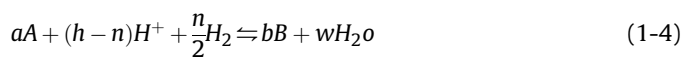
At potentials more negative than the equilibrium potentials for hydrogen oxidation reaction (A), it is thermodynamically possible to evolve hydrogen. Likewise, at potentials higher than equilibrium potentials for oxygen reduction reaction (B), it is thermodynamically possible for the evolution of oxygen to occur. As the pressure of the gaseous component increases, the equilibrium potentials for hydrogen oxidation (A) and oxygen reduction reaction (B) become more negative and positive, respectively, i.e. it becomes thermodynamically more difficult to decompose water into oxygen and hydrogen.

Since thermodynamics can primarily encompass systems at equilibrium, the concept of equilibrium involves a process moving in the oxidation or reduction direction from the equilibrium point. In order for understanding electrochemical activities in evaluations of standard electrode potentials, thermodynamic approach for calculating the free energy change and the equilibrium potential for the generalized redox couples in an aqueous system has been well described in literatures [16–19].

In general, the following reduction reaction (1-2) and the balancing hydrogen oxidation reaction (1-3) are generally considered as;



Then, the overall redox reaction is;



For an electrode reaction, equilibrium is characterized by the Nernst equation and an equilibrium potential for the overall redox reaction can be calculated as;

$$E_{A/B} = E_{A/B}^0 - \frac{RT}{nF} \ln \left(\frac{a_B^b}{a_A^a a_{H^+}^h} \right) \quad (1-5)$$

The concentration of pure, solid substances is always treated as unity ($a_{H_2O} = 1$) and by utilizing $pH = -\log a_{H^+}$ and the usual values of each definition, $F = 96,487$ C/equivalent, $R = 8.3143$ J/(mole.K), and T in degree K, one can rewrite Equation (1-5) at 300 °C as;

$$E_{A/B} = E_{A/B}^{\circ} - 0.11372 \left(\frac{h}{n}\right) pH - \frac{0.11372}{n} \log \left(\frac{f_B^b}{f_A^a}\right) \quad (1-6)$$

If the system reaches a point where there is no net change of free energy (e.g., the system is in equilibrium), a standard potential, $E_{A/B}^{\circ}$, for an overall redox reaction (1-4) is expressed with a standard free energy change, ΔG° as;

$$E_{A/B}^{\circ} = -\frac{\Delta G^{\circ}}{nF} \quad (1-7)$$

In dilute systems, where partial pressures approximate fugacities and $p_A + p_B = P$, then the equilibrium potential/pH condition for equal fugacities, $p_A = p_B = \frac{P}{2}$, depends on pressure if $a \neq b$;

$$E_{A/B} = E_{A/B}^{\circ} - 0.03352 \left(\frac{b-a}{n}\right) - 0.11372 \left(\frac{h}{n}\right) pH - 0.11372 \left(\frac{b-a}{n}\right) \log P \quad (1-8)$$

For example, the potential, vs. standard hydrogen electrode (SHE) of hydrogen electrode, $H_2 = 2H^+ + 2e^-$, at a given temperature (T), can be calculated by using the Nernst equation given as;

$$E_{H^+/H_2}(T) = E_{H^+/H_2}^{\circ}(T) - 2.303 \frac{RT}{nF} [\log f_{H_2} + 2pH] \quad (1-9)$$

The hydrogen fugacity in Equation (1-9) can be determined, as follows;

$$f_{H_2} = H_{H_2} \cdot a_{H_2(aq)} \quad (1-10)$$

The hydrogen fugacity has the relationship with the activity of hydrogen in water. Dependence of temperature on the Henry's law constant for hydrogen, H_{H_2} , can be found in literatures [20,21]. Then, Equation (1-9) for the hydrogen electrode potential at 300 °C can be rewritten as;

$$E_{H^+/H_2}(300^{\circ}C) = -0.114pH - 0.056(f_{H_2}) \quad (1-11)$$

With same approaches for O_2 and H_2O_2 in 300 °C pure water, the potentials vs. concentrations for O_2 and H_2O_2 can be also calculated using the following relations, respectively;

$$E^{\circ}(O_2 / H_2O) = 1.022 - 0.114pH + 0.028(f_{O_2}) \quad (1-12)$$

$$E^{\circ}(H_2O_2 / H_2O) = 1.772 - 0.114pH - 0.056(a_{H_2O_2}) \quad (1-13)$$

A comparison of calculated electrochemical potentials of hydrogen, oxygen and hydrogen peroxide reactions at various concentrations in 288 °C pure water (pH = 5.67) is shown in Fig. 1 [15] and the plot at 300 °C should be very close to Fig. 1.

H_2O_2 is known to act not only as an oxidizing agent with formation of water but also as a reducing one with formation of oxygen that creates a large potential domain of spontaneous instability, as illustrated in Fig. 2 in 288 °C pure water [14,15]. The oxidation reaction and reduction reaction of H_2O_2 are, respectively;



If H_2O_2 is in contact with a metallic surface whose electrode potential is in the instability region, H_2O_2 can spontaneously decompose into water and oxygen according to the following reaction:

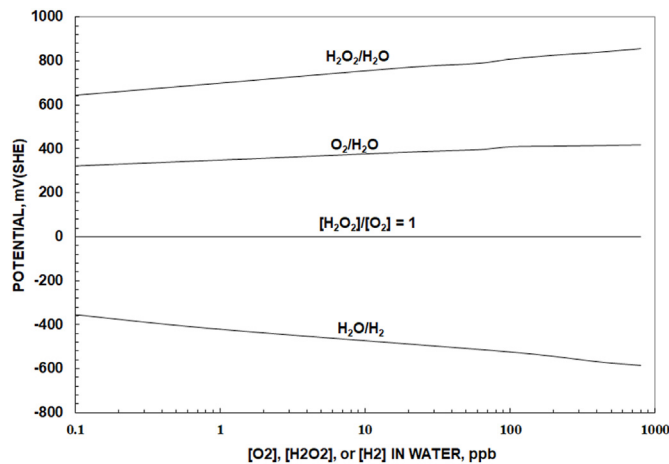


Fig. 1. Redox potential of $H_2/O_2/H_2O_2$ couples in 288 °C water containing different concentrations of dissolved hydrogen, oxygen, and hydrogen peroxide.



However, the decomposition of H_2O_2 into water and oxygen may not be possible if an electrode potential does not lie within this unstable region.

3. Electrochemistry and thermodynamic stability of nitrogen species in high temperature water

When the reaction involves a change in oxidation state, it is convenient to consider the oxidation and reduction reactions separately since redox reactions can occur physically in different locations and are amenable to external control by applied electrical potential difference. Potential differences are related to free energy changes involved in processes occurring in an electrochemical system. Consideration of the mechanisms for establishing potential differences proves insights for examining the active control of potentials in a given electrochemical system.

Since no reliable thermodynamic data for ionic species at temperatures above 25 °C is available, the thermodynamic relationship is driven and applied to calculate the change in free energy from each chemical potential at the temperature as;

$$\mu(T_2, P_2) = \mu(T_1, P_1) + \int_{P_1}^{P_2} \bar{V} dP + \int_{T_1}^{T_2} \bar{C}_p dT - T_2 \int_{T_1}^{T_2} C_p d \ln T - (T_2 - T_1) \bar{S}(T_1, P_1) \quad (2-1)$$

where μ is the molar free energy for pure substances and the partial molar free energy for ions in solution at temperature. V , C_p , and S are the volume, heat capacity and entropy, respectively, for a given substance at constant pressure. Value of $\mu(T_i, P_i)$ for ions in solution and pure compounds is then used for calculation of the molar Gibbs free energy. More detail of theoretical approaches for driving the relationship (2-1) has been well described elsewhere [16–18].

The most convenient approach for thermodynamic calculations of a specific substance at a given temperature is generally made with the heat capacity at constant pressure in the empirical equation form [16,17];

$$\bar{C}_p^{\circ} = A + BT + CT^{-2} \quad (2-2)$$

Assuming the standard states for gases is the pure ideal gas at unit pressure and the molar volume change of liquids and solids

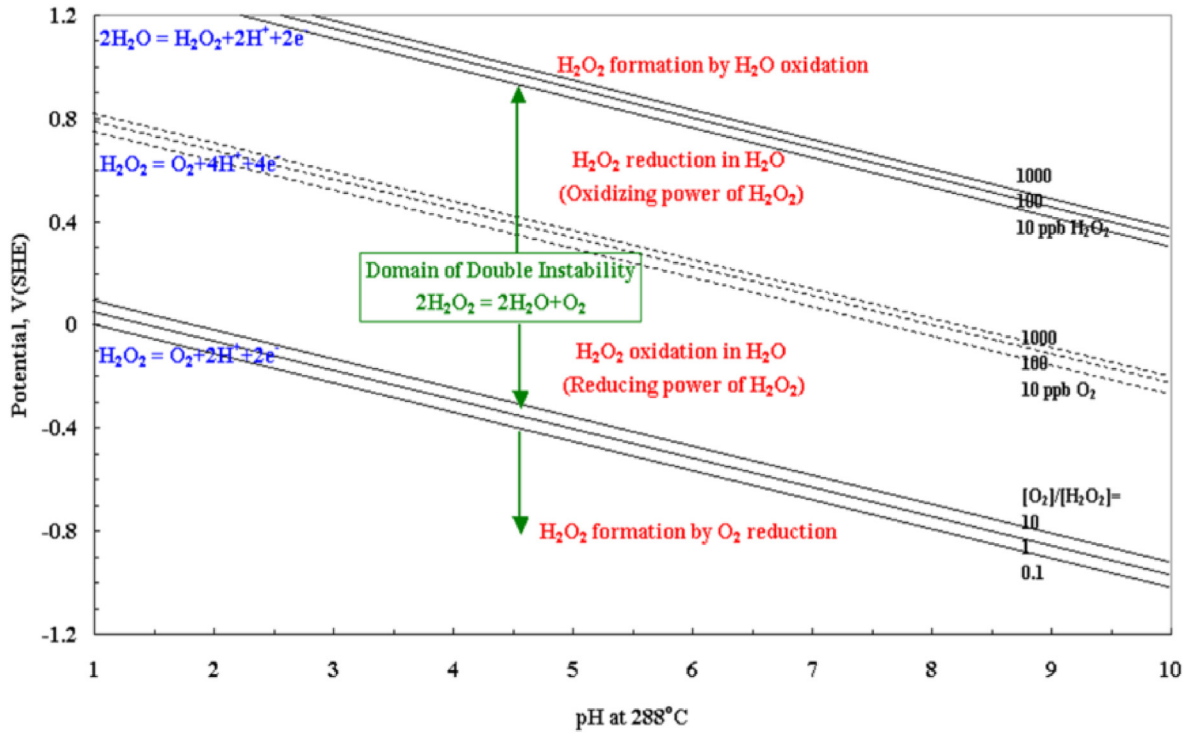


Fig. 2. Potential-pH equilibrium diagram of H₂O₂ and O₂ in 288 °C pure water.

with pressure is not significant, then combining the relationships (2-1) and (2-2) and followed by its integration lead to the following relation;

$$\begin{aligned} \mu^\circ(T_2) = & \mu^\circ(T_1) + A \left[T_2 - T_1 - T_2 \ln \frac{T_2}{T_1} \right] + B \left[T_2 T_1 - \frac{T_2^2}{2} - \frac{T_1^2}{2} \right] \\ & + C \left[\frac{1}{T_1} - \frac{1}{2T_2} + \frac{T_2}{2T_1^2} \right] - (T_1 - T_2) \bar{S}^\circ(T_1) \end{aligned} \quad (2-3)$$

Thus, the relationship (2-3) leads to the calculation of chemical potential of any component at temperatures or pressures if the chemical potential of component in its standard state at 25 °C and 1 atm is known.

With molar heat capacity data available for many pure substrates at 25 °C in literatures [16,18,19], heat capacity values of various nitrogen species at higher temperatures can be calculated. NH₃ is known to behave least like an ideal gas, but has been treated as an ideal gas at temperatures above boiling point for calculating its thermodynamic properties at high temperatures [22–24].

Table 1 summarizes the thermodynamic data of μ° (25 °C), S° (25 °C) and constant values of C_p° for nitrogen species and other molecules. The calculated values of μ° at 300 °C are also provided.

It has been reported that the possible nitrogen species in water can exist in several chemical forms such as N₂O₄, NO₂, NO, N₂O, N₂, and NH₃ from the highest and lowest oxidation state [10]. Then, in order for determining the thermodynamic stability regions for nitrogen species, the possible redox couples of nitrogen compounds with the hydrogen oxidation reaction (A) for the H⁺/H₂ couple (H₂ = 2H⁺ + 2e⁻) as a reference oxidation reaction are listed in Table 2. In order to predict the thermodynamic stability of coupled nitrogen species in LWR water chemistry, accurate calculated values on free energy change and equilibrium potential for the redox reactions of possible nitrogen compounds are needed.

The free energy change for the overall redox reaction (2-3) in an aqueous system then can be calculated for chemical couples using the following formula as;

$$\Delta G^\circ = b\mu_B^\circ + W\mu_{H_2O}^\circ - (h - n)\mu_H^\circ + \frac{n}{2}\mu_{H_2}^\circ \quad (2-4)$$

Table 1
Thermodynamic data of various species at 25 °C and 300 °C.

Chemical Species	μ° (25 °C), (cal/mole)	S° (25 °C), (cal/mole-K)				μ° (300 °C), (cal/mole)
			A	B (10 ⁻³)	C (10 ⁵)	
NH ₃	-4000	45.96	7.11	6.00	-0.37	-17,547
N ₂	0	45.77	6.66	1.02	0.00	-13,289
N ₂ O	24,700	52.80	10.92	2.06	-2.04	9,166
NO	20,700	50.34	7.03	0.92	-0.14	6,132
NO ₂	12,400	57.46	10.26	2.04	-1.61	-4,381
N ₂ O ₄	23,500	72.73	20.05	9.50	-3.56	1407
H ₂	0	31.22	6.52	0.78	0.12	-9,273
H ₂ O	-56,720	16.75	18.03	0.00	0.00	-63,122
O ₂	0	49.01	7.16	1.00	-0.40	-14,199

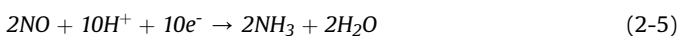
Table 2
Calculated thermodynamic values for various nitrogen redox couples in 300 °C high purity water.

Redox Couple	Free Energy Change ΔG° , calories	Standard Potential E° , V vs. SHE(T)	Redox Potential E , V vs. SHE(T)	
			$P = 8.5 \times 10^{-7}$ atm	$P = 1$ atm
$N_2O + H_2 = N_2 + H_2O$	-76,304	1.654	1.003	1.003
$2NO + 2H_2 = N_2 + 2H_2O$	-133,250	1.445	0.624	0.794
$N_2O_4 + 3H_2 = N_2O + 4H_2O$	-216,911	1.568	0.917	0.917
$2NO + H_2 = N_2O + H_2O$	-56,947	1.235	0.244	0.584
$2NO_2 + 4H_2 = N_2 + 4H_2O$	-219,923	1.192	0.456	0.541
$N_2O_4 + 3H_2 = N_2O + 3H_2O$	-153,788	1.111	0.461	0.461
$N_2O_4 + 2H_2 = 2NO + 2H_2O$	-96,842	1.050	0.569	0.399
$2NO_2 + 3H_2 = N_2O + 3H_2O$	-143,619	1.038	0.274	0.387
$NO_2 + H_2 = NO + H_2O$	-43,336	0.940	0.289	0.289
$N_2O_4 + 7H_2 = 2NH_3 + 4H_2O$	-224,076	0.694	0.091	0.043
$2NO_2 + 7H_2 = 2NH_3 + 4H_2O$	-213,907	0.663	0.012	0.012
$2NO + 5H_2 = 2NH_3 + 2H_2O$	-127,235	0.552	-0.099	-0.099
$N_2O + 4H_2 = 2NH_3 + H_2O$	-70,288	0.381	-0.186	-0.270
$N_2 + 3H_2 = 2NH_3$	6,016	-0.043	-0.582	-0.694

The value of free energy change (ΔG°) can be calculated using the thermodynamic value of each species listed in Table 1 into Equation (2-4).

The standard potential (E°) and redox potential (E) for equal fugacities among the nitrogen species in 300 °C high purity water ($pH = 5.71$) then can be calculated by Equations (1-7) and (1-8) and are summarized at Table 2. Redox reactions listed in Table 2 have the same dependence on pH since $n = h$, but not on partial pressure when $a = b$. On the other hand, in case of $a \neq b$, the potential/ pH condition for equal fugacities depends on pressure (e.g., fugacity) and thus the solubility values in water at 300 °C are required for the pressure-dependent terms in Equation (1-8). Based on limited solubility data for N_2 in water at high temperatures [25,26], a fugacity of $\sim 8.5 \times 10^{-7}$ atm ($P = 8.5 \times 10^{-7}$ atm) in 300 °C water was estimated and used for calculating the redox potentials of reactions with $a \neq b$ and the potentials at a fugacity of 1 atm ($P = 1$ atm) were also calculated for comparison.

As an example for calculating thermodynamic values of NO/NH_3 redox couple listed in Table 2, the following reduction reaction of NO/NH_3 couple with the balancing hydrogen oxidation is illustrated as;



Then, the overall reaction is;



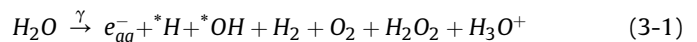
Thus, one can calculate the thermodynamic values of the free energy change by Equation (2-4), equilibrium potential by Equation (1-7) and redox potential by Equation (1-8) for the redox reaction (2-7).

Redox potentials for some nitrogen redox couples in 300 °C water are plotted in Fig. 3, along those with H_2 , O_2 , and H_2O_2 reactions. The stability limits of hydrogen oxidation reaction (A) and oxygen reduction reaction (B) in 300 °C water define the potential range of practical thermodynamic interest. It clearly indicates that N_2 is the predominant, thermodynamically stable species within LWR ranges. At room temperature, the oxidation of NH_3 to N_2 and the reduction of NO to N_2 do not occur readily. Similarly, N_2O is relatively unreactive at room temperature and decomposes irreversibly to nitrogen and oxygen as temperature increases. In addition, the instability of H_2O_2 in a wide range of potential within the LWR operation condition (see Fig. 2) should have no or minor

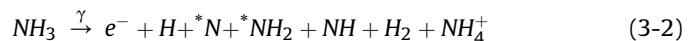
effect on the reduction of NO to NH_3 .

4. Chemical behaviors of nitrogen species under irradiation

Radiolysis of water is the process of the dissociation of water molecules by various types of ionizing radiation (α , β , γ). Several chemical species are produced by interaction of high energy radiation as a γ -radiation in water and primary products include;



Since various ion/molecule reactions and decomposition of excited molecules occur by the γ -irradiated ammonia, the effects of radiation on nitrogen species and their impacts on controlling the radiation activities in LWRs have been extensively investigated [10,27–30]. The major primary products of ammonia under γ -irradiation are;



Under a high radiation fields, nitrogen atoms (*N) are then expected to react with other species initially for forming various nitrogen species, and some reactions are [10];



Subsequently, the following reactions may occur;



Thus, under oxidizing conditions (e.g., oxygen), more $N O_3^-$ and $N O_2^-$ expect to be formed. In reactor water containing the low concentration of ammonia, ammonia will also be converted to

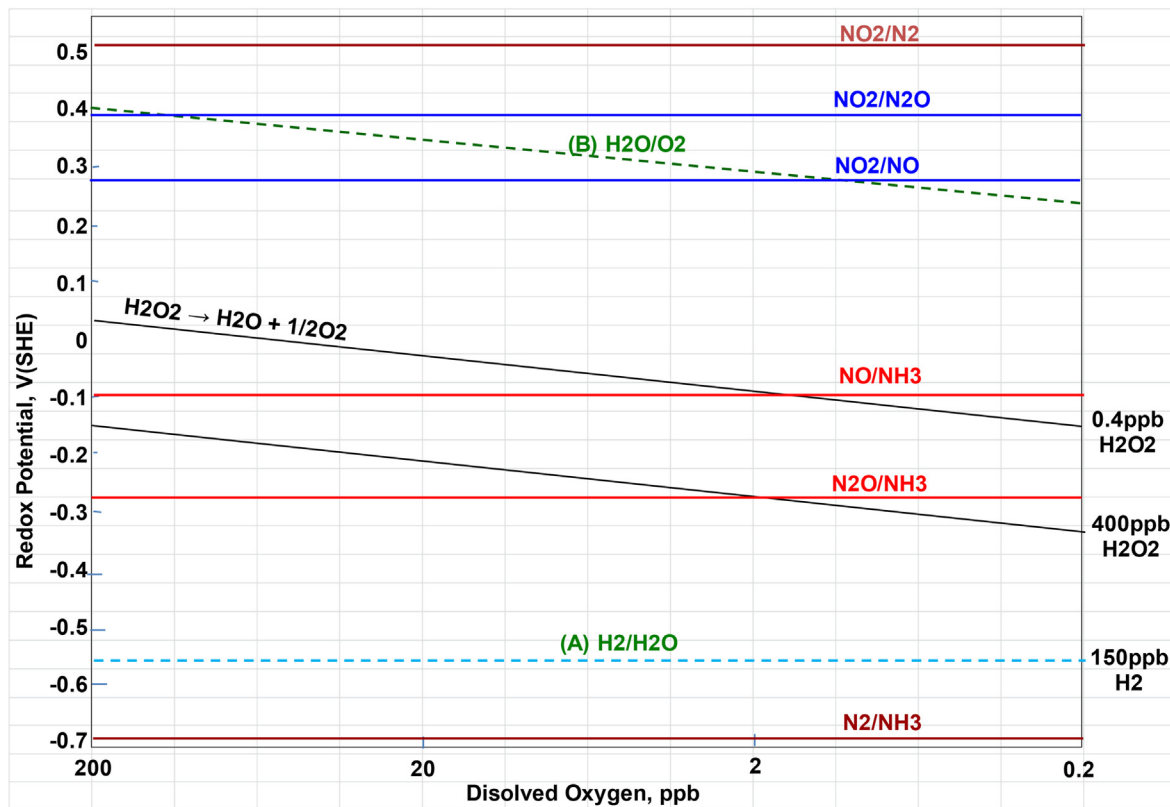


Fig. 3. Thermodynamic relationship of H₂, O₂, H₂O₂ and nitrogen redox couples (P = 1 atm) in 300 °C water.

nitric acid in the reactor core by the following reactions;



On the other hand, in the presence of hydrogen, more NH₃ is expected to form as most of the oxidizing species are eliminated. Although N₂ is thermodynamically stable, its formation from two nitrogen atoms at very low concentrations in reactor coolant is very unlikely. However, in water containing N₂, major radiolytic products are known to be N O₂⁻, N O₃⁻, and NH₃. In oxygenated system (e.g., O₂ and H₂O) by the depletion of nitrogen as compared to pure nitrogen system, the yield of N O₃⁻ is negligible due to unavailability of nitrogen source.

The dependence of dose rate on the product concentration of nitrogen species (N O₃⁻, NH₃) has been extensively investigated, as shown in Fig. 4 [27]. At lower dose rate, the yield of N O₃⁻ is very similar both in aerated and N₂-purged water, while with increase in dose, all nitrogen products initially increase and reach a plateau value at 450 kGy dose. The formation of ammonia is observed only at high doses. The difference growth rate of NH₃ and N O₃⁻ concentration has been proposed to the different reaction mechanisms as a direct reaction of N₂ with ^{*}OH radicals (reaction 3-15) and a reaction of N₂ with excited water molecules (reaction 3-16) for nitrate formation, respectively;

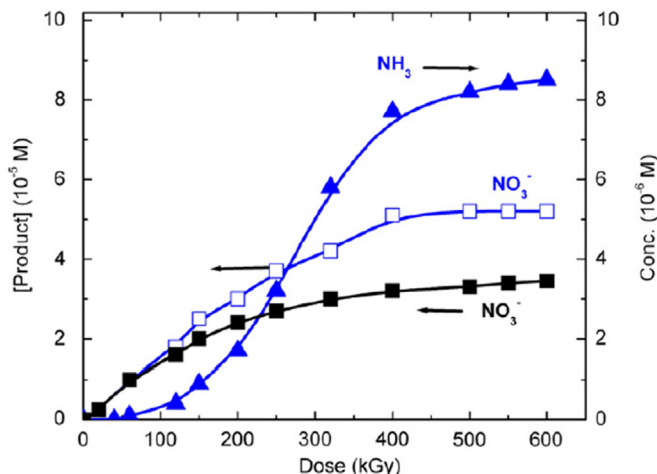


Fig. 4. Plot of the variation of the product concentrations with γ -irradiation dose in aerated (-■- N O₃⁻) and nitrogen-purged (-□- N O₃⁻ and -▲- NH₃) water at natural pH [27].

The nitrogen behavior in oxygen or hydrogen water system in the presence of nitrogen under irradiation were present has been well studied [28,31]. Fig. 5 shows the effect of γ -irradiation on the radiochemical production of nitrogen species in water containing nitrogen either in the presence of oxygen or hydrogen has been investigated [28]. It is clearly shown that the γ -irradiation of N₂-O₂-H₂O system produced only N O₃⁻, but no NH₄⁺ was detected, indicating the effect of N₂ concentration radically produced N O₃⁻ concentration. While in irradiated N₂-H₂-H₂O system, both N O₃⁻

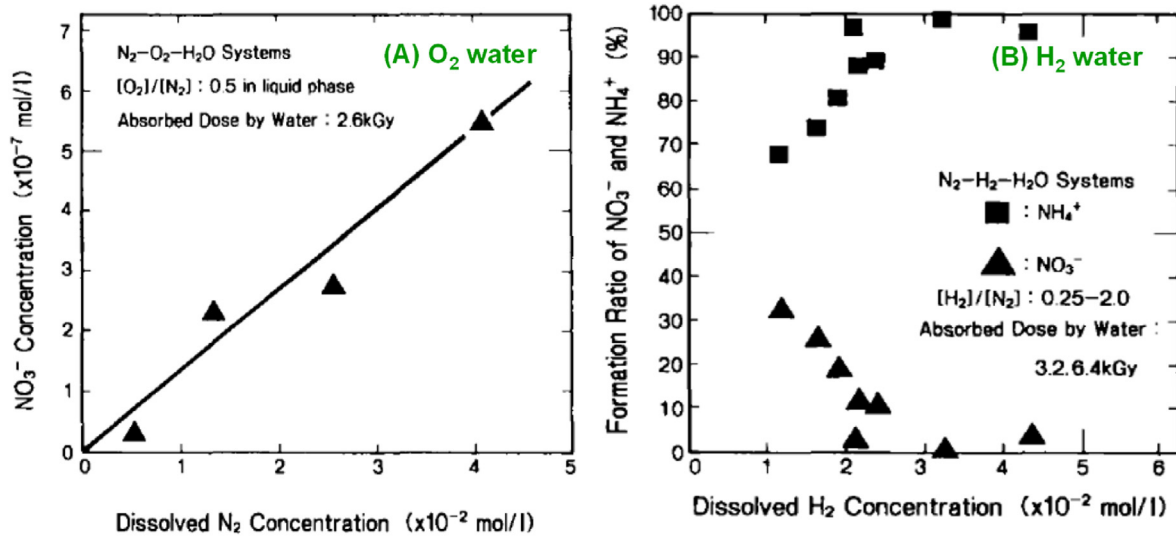


Fig. 5. (A) Production of NO₃⁻ vs. N₂ concentration in irradiated N₂-O₂-H₂O system and (B) production of NO₃⁻ and N H₄⁺ vs. N₂ concentration in irradiated N₂-H₂-H₂O system [28].

and NH₄⁺ were detected. However, the production ratio of N O₃⁻ decreased with increasing hydrogen concentration, while the opposite behavior on the production ratio of NH₄⁺. Thus, it is evident that the production ratio of NO₃⁻ and NH₄⁺ strongly depends on the dissolved oxygen and hydrogen concentration; more NO₃⁻ production in O₂ water and more N H₄⁺ in H₂ water.

5. Chemical behaviors of ammonia in nuclear reactor coolant

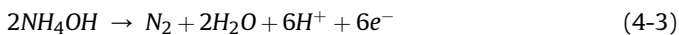
Ammonia is added to the primary coolant at VVERs as a hydrogen source by the radiolytic decomposition of ammonia to suppress radiolysis in-core. In addition to ammonia, hydrazine is also used to achieve hydrogen concentration in the primary coolant, thermodynamically and/or radiolytically, decomposed to ammonia, nitrogen and hydrogen;



When hydrazine is in coolant containing oxygen, it also slowly oxidizes with the net reaction:



Since nitrogen is not thermodynamically stable outside lines of hydrogen oxidation reaction (A) and oxygen reduction reaction (B), one of thermodynamically possible oxidation reactions of ammonia with many hydrolysis reactions is;



The following reduction reactions in-core regions can be expected by the water radiolysis;



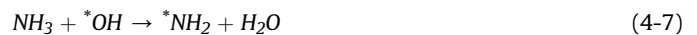
Thus, two overall redox reactions can be driven by the different reduction potentials for reaction (4-4) at low potential and for oxygen reduction reaction (B) at high potentials, respectively;



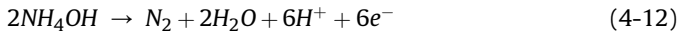
It is now clearly evident that within the hydrogen oxidation and oxygen reduction domains, N₂ is thermodynamically stable if no external force is applied to the system.

It has been well studied that the γ -irradiation of aerated ammonia solution leads to the formation of N O₂⁻ and its yield increases with increase in concentration of ammonia [32–34]. As the rate constant for the reaction of *OH radicals with ammonia is not very high, a relatively higher concentration of ammonia is required to scavenge all the *OH radicals due to the competing reactions of *OH radicals with e_{aq}⁻, H and *OH radicals themselves. An increase in the concentration of NH₃ increases its reactivity with *OH radicals, thus leading to an increase in the yield of *NH₂ radicals and ultimately N O₂⁻. However, at very high concentrations of NH₃, spur scavenging of the *OH radicals may also lead to higher yields of N O₂⁻.

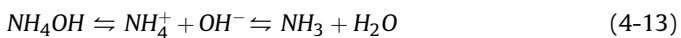
An increase in the O₂ concentration can also give rise to an increase in the yield of N O₂⁻ due to favorable competition of reactions below with the dimerization reaction of *NH₂ radicals [30];



As illustrated above for various redox reactions of nitrogen chemicals, a comprehensive thermodynamic analysis of the N₂-H₂O system reveals electrochemical reactions of N H₄⁺ - NH₄OH - NHO₂ - N O₂⁻ - HNO₃ - NO₃⁻ at the ambient temperature [10–12]. Although the complete chain reactions are very complicate, it is noteworthy that the domain of N₂ almost completely covers the stable domain of water as illustrated in Fig. 3. It is also shown that nitrogen is not thermodynamically stable under conditions of pH and electrode potential lying outside lines for hydrogen potential and oxygen potential. Consequently conditions are obtained under which the fixation of nitrogen gas in the form of an ammonia solution is thermodynamically possible according to the following reactions (4-10) to (4-12):



However, considering the irreversibility, nitrogen is practically not oxidized and not reduced in a solution. The observation that ammonia is decomposing into H_2 and N_2 indicates that the oxidation of ammonia is possible by reactions (4-11) and (4-12), which are reverse reactions of the fixation of nitrogen. It is also known that the semi-volatile NH_3 is always in equilibrium with NH_4OH according to the following reaction (4-13);

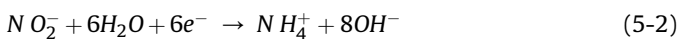
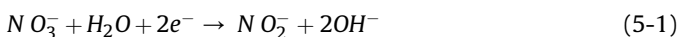


Apparently, with increasing the pH of water (e.g., at high OH^- concentrations), more volatile form of NH_3 will be generated and the water pH may be eventually increased and the nitrogen chemistry equilibrium may shift as a result.

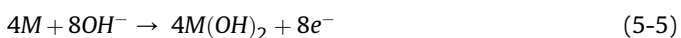
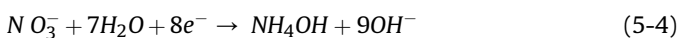
6. Effect of nitrogen species on crevice chemistry in high temperature water

Crevice corrosion is one of many key failure modes on materials occurring at LWRs during long-term service. Crevice corrosion has been observed in occlude regions with a long incubation time before failure due to the presence of geometric crevices. Depletion of oxygen and significant different ionic concentration can exist within the crevice. Thus, the crevice chemistry containing nitrate ions expects to affect the corrosion kinetics and oxidation behavior of structural alloys in high temperature water.

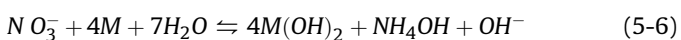
In the absence of oxygen, no concentration cell mechanism can operate and N O_3^- reacts directly with alloys, M , to produce an excess of OH^- ;



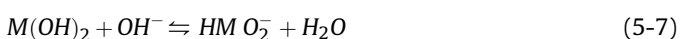
Nitrogen must be reduced beyond the +3 oxidation state or the water in the crevice will remain only slightly basic, with the excess hydroxyl ions (OH^-) balanced electrically by metal cations (M^{+n}) and the pH limited by the solubility of the metal hydroxides. However, if the second reduction also occurs, the strong caustic water can result;



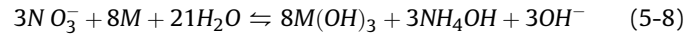
The overall reaction is then;



where, for this divalent metal system, the pH is limited by the formation of oxy-anions;

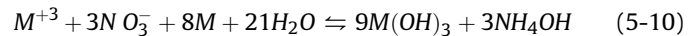
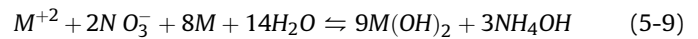


A trivalent metal produces a similar result;



but, apparently only chromium forms soluble oxy-anions which regulates the pH [8–10].

In the presence of oxygen or other oxidizing agencies, the pH must be lower since some portion of N O_3^- are then balanced electrically by M^{+n} or H^+ . The pH would be limited to neutral or slightly basic values by hydroxide solubility with at least one of metal cations and no charge transported to divalent or trivalent metal cations;



Thus, N O_3^- can produce very alkaline crevice water at high temperature by direct reactions to corrosion of metals which occurs in the crevice, and only when the concentration of impurity cations is sufficiently high. Nevertheless, slightly acidic pH values would be also attained if the excess N O_3^- reacts completely and hydrolysis occurred

7. Effect of nitrogen species on IGSCC in high temperature water

Environmental factors affecting the IGSCC susceptibility of materials (e.g., Fe or Ni based alloys) and the potential consequences of components failures by IGSCC in high temperature water have been studied for many years [5–8]. In particular, standard design criteria of materials requires specific mechanical properties for current and proposed future nuclear energy systems that provide adequate resistance to overarching environmental degradation phenomena (e.g., radiation damage and chemical compatibility). Since the chemical compatibility issues (corrosion, SCC, etc.) are largely dependent on the specific coolant and engineering application, a lot of efforts have been devoted to examination of environmental factors (e.g., water chemistry, temperature, impurities, flow rate, etc.).

Among several environmental factors, oxygen is known to be the most powerful species for enhancing the IGSCC susceptibility of materials in high temperature water. However, there are very limited literatures describing the effects of specific ions such as sulfates (S O_4^{2-}), carbonates (HC O_3^-), nitrates (N O_3^-), and fluorides (F^-) that can contribute to the water conductivity and perhaps facilitate IGSCC. In addition, SCC of alloys may also occur by a mechanism which is closely related to caustic cracking, and ought to be more severe with higher salt concentrations and lower oxygen.

Chloride (Cl^-) has also a well-known accelerating effect on the IGSCC process [35–38], while nitrate tends to reduce the IGSCC susceptibility at low corrosion potential (in the presence of oxygen) in the O_2 depleted crack or crevice by forming ammonia ($\text{N O}_3^- \rightarrow \text{N O}_2^- \rightarrow \text{N H}_4^+$). Nitrate is the highest oxidation state for nitrogen and does not easily hydrolyze in high temperature water. At LWRs, the nitrate concentration is typically managed to be < 0.5 ppb in reactor coolant. Since nitrate is reduced in low corrosion potential environments, no effects of nitrate on IGSCC propensities are anticipated under HWC condition (reducing hydrogen water chemistry), as shown in Fig. 6, comparing with the data measured in NWC (oxidizing oxygen water) [36]. Thus, in the presence of hydrogen, nitrate may not additionally contribute to the IGSCC behavior of materials in high temperature water. However, more investigation is needed for a better understanding of important role of several

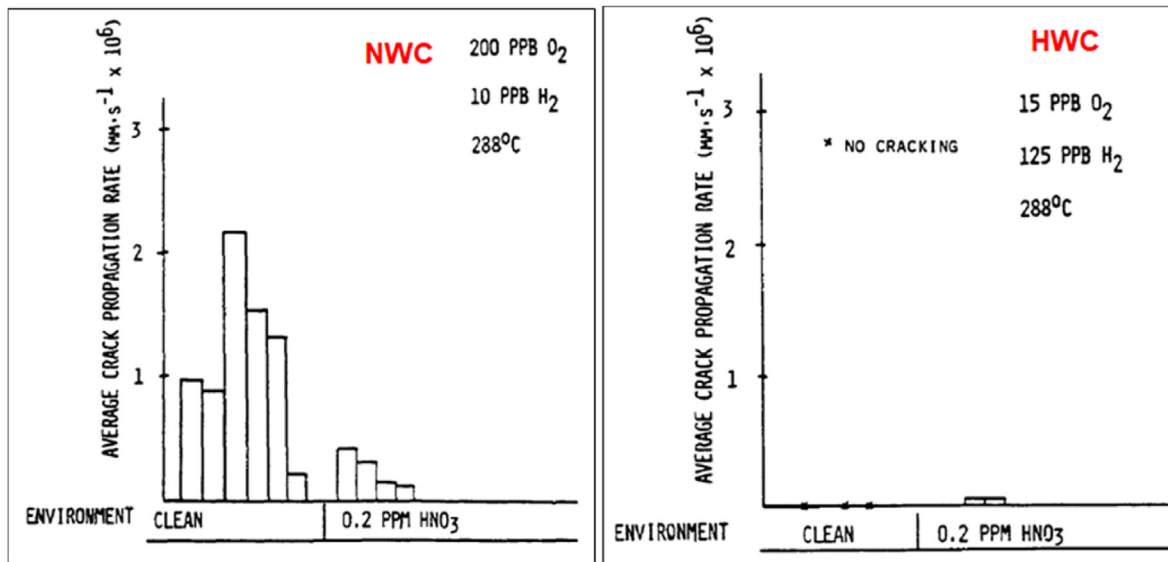


Fig. 6. Effect of nitrate on IGSCC of sensitized 304SS in oxidizing water (NWC) and reducing water (HWC) at 288 °C [36].

anionic impurities together, such as chloride, sulfate, chromate (Cr O₄²⁻), etc.

Effect of nitrate on the crack growth rate (CGR) of sensitized 304SS in oxidizing water at 288 °C was examined [37]. It was found that at levels up to at least 100 ppb nitrate there were no perceptible effects, shown in Fig. 7. Author postulated that nitrate is drawn into the crack by the gradient in corrosion potential (e.g., by the oxygen concentration gradient) become cations, which are drawn out of the crack. Also, acidification does not occur because of the formation of hydroxide during the reduction to form ammonia. Thus, the concentration of nitrate is limited by their reduction to ammonia and transport back out of the crack. Acidification does not occur because of the formation of hydroxyl ions, and pH buffering occurred because of the ammonia (NH₃)-ammonium (N H₄⁺) equilibrium. However, the CGR test has to be performed in the absence of oxygen by eliminating the factor of corrosion potential gradient

from the crack mouth to the crack tip for a specific role of nitrate only.

As stated previously, ammonia is added into the VVER primary feed water for maintaining hydrogen concentration and removing dissolved oxygen. It was also reported that a great amount of stress corrosion cracking, pitting corrosion and mechanical damage was observed at various locations at the reactor pressure vessel and the primary circuit coolant systems [38]. Most of corrosion damages generally occurred on local increase in chloride aggressiveness in the region of the welding joint and between heat exchanger tubes, but not related to the nitrogen species from ammonia, mainly due to relatively low levels of nitrogen species under the reducing condition, as demonstrated in Fig. 6. Furthermore, even in oxidizing water, a low level of nitrogen species may not contribute significantly to the material degradation since more detrimental effect from oxygen is expected.

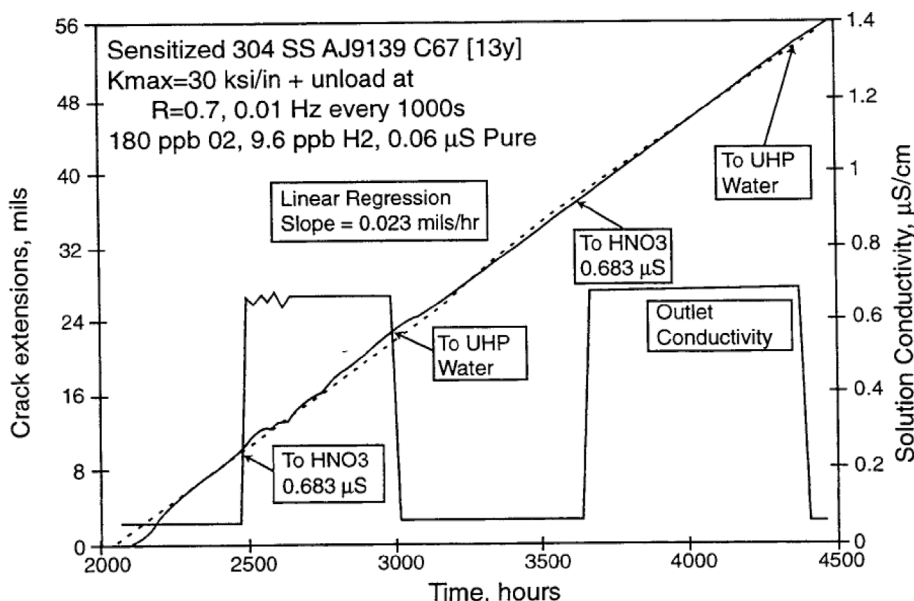


Fig. 7. Crack extension vs. Time for CT specimens of sensitized 304SS showing minimum effect of 100 ppb nitrate (as HNO₃) on crack growth rate in 288 °C water [37].

8. Summary

Radiochemical behaviors of water and ammonia are described for the extent of basic understanding of interactions of various chemical species in LWR coolants. Radiolysis of in-core water coolant produces several radicals and ionic/molecular species, and the ammonia radiolysis also generates dozens of radioactive nitrogen species, with uncertainty of their stabilities and domains in reactor water environments. When an interaction of radicals with other radioactive species occurs in the coolant system, a change in oxidation/reduction states of ionic/molecular species can occur thermally or radiolytically at different locations.

Therefore, it is very important to understand the chemical behavior of radiolytic products (e.g., O_2 , H_2 , and H_2O_2) and nitrogen species in high temperature water, but high temperature thermodynamic data are not available to predict redox behaviors and stabilities of chemical species in LWR water. Thermodynamic consideration of chemical species is indeed necessary for calculating the chemical potentials related to free energy changes of such species for a better understanding of their stabilities and chemical interactions in high temperature water. This can be perceived with both heat capacity and standard electrode potential at elevated temperatures using the entropy correspondence principle, and then thermodynamically stable species and their domains within the operating LWR condition can be predicted. On the basis of heat capacity approximation at low temperatures, thermodynamic values of the free energy change (ΔG^0), the standard electrode equilibrium potential (E^0) and the redox potential (E) for redox reactions of various chemical species and nitrogen compounds in 300 °C pure water are calculated. Calculated values of redox potentials for nitrogen species clearly indicates that N_2 is the predominant, thermodynamically, stable species within the LWR operating condition.

The ammonia radiolysis generates hydrogen by the radiolytic decomposition reaction, $2NH_3 \rightarrow 3H_2 + N_2$ that with some extent, leads to the formation of $N O_2^-$ ions by reacting with oxygen, and the yield of $N O_2^-$ depends on the pH of ammonia solutions and the O_2 contents. It was clearly shown that under oxidizing conditions (e.g., oxygen) containing ammonia or nitrogen species, more $N O_3^-$ and $N O_2^-$ are formed, while in the presence of hydrogen, more NH_3 . Thus, the production ratio of $N O_3^-$ and $N H_4^+$ strongly depends on the dissolved oxygen and hydrogen concentration; more $N O_3^-$ production in O_2 water and more $N H_4^+$ in H_2 water.

Since nitrate does not easily hydrolyze in high temperature water, it can enter into the crack tip as an ionic form. The presence of nitrate at the crack tip may be beneficial to material performance by raising the pH level, enhancing the repassivation kinetics, and consequently alleviating the degradation of materials. In general, a low concentration of nitrogen species (e.g., in ppb level) under hydrogen water chemistry condition (e.g., low corrosion potential) may not be detrimental significantly on material performance. Nevertheless, an accumulation of nitrogen species at some locations (e.g., deep crevices or crack tips) may create the different water chemistry condition (e.g., local pH change) that may enhance the corrosion kinetics and SCC susceptibility of components. However, regardless of nitrate presence, oxygen should be avoided for minimizing the corrosion potential gradient through the crack/crevice depth.

Declaration of competing interest

The authors declare that they have no known financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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