



Review

A Critical Review of Radiolysis Issues in Water-Cooled Fission and Fusion Reactors: Part I, Assessment of Radiolysis Models [†]

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Abstract: A critical review is presented on modeling of the radiolysis of the coolant water in nuclear power reactors with emphasis on ITER. The review is presented in two parts: In Part I, we assess previous work in terms of compliance with important chemical principles and conclude that no model proposed to date is completely satisfactory, in this regard. Thus, some reactions that have been proposed in various radiolysis models are not elementary in nature and can be decomposed into two or more elementary reactions, some of which are already included in the models. These reactions must be removed in formulating a viable model. Furthermore, elementary reactions between species of like charge are also commonly included, but they can be discounted upon the basis of Coulombic repulsion under the prevailing conditions ($T < 350\text{ }^{\circ}\text{C}$) and must also be removed. Likewise, it is concluded that the current state of knowledge with respect to radiolytic yields (i.e., G-values) is also unsatisfactory. More work is required to ensure that the yields used in radiolysis models are truly “primary” yields corresponding to a time scale of nanoseconds or less. This is necessary to ensure that the impact of the reactions that occur outside of the spurs (ionizing particle tracks in the medium) are not counted twice. In Part II, the authors review the use of the radiolysis models coupled with electrochemical models to predict the water chemistry, corrosion potential, crack growth rate in Type 304 SS, and accumulated damage in the coolant circuits of boiling water reactors, pressurized water reactors, and the test fusion reactor, ITER. Based on experience with fission reactors, the emphasis should be placed on the control of the electrochemical corrosion potential because it is the parameter that best describes the state of corrosion in coolant circuits.

Keywords: radiolysis of water; water-cooled reactor coolant circuits; ITER

1. Introduction

Like many of its fission counterparts, a fusion reactor will employ light water (i.e., H_2O) to transfer heat from the Tokamak (i.e., plasma) to a boiler to produce the steam that will then drive conventional steam turbines to produce electrical power. ITER (“the way” in Latin) is not designed to produce electricity on a commercial scale; instead, it is intended to demonstrate sustained plasma burn and hence the feasibility of fusion power. Like most fission reactors, it too will be cooled by light water. The water will spend a certain time in the plasma radiation zone, in which the water will be subjected to intense, high-energy n and γ ionizing radiation. In the tritium breeding blanket containing LiOH , α radiation and tritons will be produced via the reaction ${}^6\text{Li}_3({}^1\text{n}_0, {}^4\text{He}_2){}^3\text{H}_1$, and these high

Linear Energy Transfer (LET) radiation forms must be included in the source term for the radiolytically-generated species. This review is concerned primarily with water radiolysis in the IBED PHTS (Integrated FW [First Wall]/BLK [Blanket]/ELMS [Edge Localized Mode and Vertical Stabilization Coil]/DIV [Divertor] Primary Heat Transfer System), which is one of the loops of the Tokamak Cooling Water System (TCWS) of the ITER [1]. However, where necessary, reference will be made to previous radiolysis/ECP/crack growth rate studies in Boiling Water Reactors (BWRs) and Pressurized Water Reactors (PWRs) (particularly in Part II). Only brief reference will be made to radiolysis in the tritium breeding blanket. Nevertheless, interaction of the ionizing radiation with the coolant (water) results in the generation of a variety of radiolysis products, with those being identified to include e_{aq}^- , H, OH, H_2O_2 , HO_2 , HO_2^- , O_2 , O_2^- , O_2^{2-} , O^- , O, H_2 , OH^- , H^+ and possibly others. These species are electroactive (i.e., they can participate in charge transfer reactions at metal/solution interfaces), thereby impacting corrosion processes and may lead to enhanced damage and to failure of components in the reactor primary coolant circuits by generating an excessively high electrochemical corrosion potential (ECP). Therefore, to understand and predict the impact of corrosion on the structural materials in the IBED PHTS of the ITER, the concentrations of these species must be known. While methods are available for measuring the concentrations of some of the radiolysis products (e.g., O_2 , H_2 , H_2O_2) in the laboratory, few techniques are presently available for measuring the concentrations of the more energetic species, such as e_{aq}^- , OH, HO_2 , O^- , O, O_2^- , O_2^{2-} and O^{2-} , all of which are present at very low concentrations, in a plant environment, although absorption spectroscopic methods are used with great success in the laboratory and might be adapted to the field. However, from an electrochemical/corrosion viewpoint, there is no pressing need for knowing the concentrations of many of these highly energetic species. This is because the contribution that any given species makes to determining the ECP and the corrosion rate is roughly proportional to its concentrations because rate of transport to the surface and the partial current density are often mass transport controlled and hence are proportional to the concentration. In performing this review, a large literature base [1–292] was consulted; however, the literature review was not exhaustive as many studies of lesser importance are not cited because of limitation of space.

For boiling water (i.e., fission) reactor (BWR) coolant circuits, the three most important species have been identified as O_2 , H_2 , and H_2O_2 , and the contributions from the highly energetic species such as e_{aq}^- , OH, H, HO_2 , O^- , O, O_2^- , O_2^{2-} and O^{2-} can be ignored for the reasons given above. This is fortunate because reliable electrochemical kinetic data, such as exchange current densities and transfer coefficients, are not available for the highly energetic species that are present at low concentration, whereas the required data for O_2 , H_2 , and possibly H_2O_2 have been obtained. In the case of pressurized water (i.e., fission) reactors (PWRs) operating with high hydrogen levels in the primary coolant, aquated electrons, OH radicals, and atomic hydrogen are predicted to be present at significant concentrations (see Figure 1) and should probably be included in the list of electroactive species. Of these species, OH is a powerful oxidizing agent, while H and e_{aq}^- are powerful reducing agents.

As noted above, no electrochemical kinetic data are available for any of these minor radiolysis species. Furthermore, H and e_{aq}^- are so overwhelmed by molecular hydrogen at the concentration that is typically present in a PWR primary coolant, as shown in Figure 1 (25 cm^3 (STP [standard temperature and pressure])/kg $H_2O \equiv 1.17 \times 10^{-3} \text{ m} \equiv 2.23 \text{ ppm}$), that they too may be combined to form an “equivalent” hydrogen species as $[H_2^*] = [H_2] + 0.5[H] + 0.5[e_{aq}^-]$, recalling that the contribution that any given species makes to the ECP is roughly proportional to its concentration. Likewise, a new hydrogen peroxide species may be defined as $[H_2O_2^*] = [H_2O_2] + 0.5[OH]$ and a new oxygen concentration as $[O_2^*] = [O_2] + 0.5[O]$. In this way, the contributions of all relevant radiolysis products are counted toward determining the ECP, general corrosion rate, and the crack growth rate (CGR) in structural materials. Even so, there is no question that the electrochemistry of a PWR primary coolant system is dominated by H_2 , but significant

contributions to the corrosion behavior of a PHTS structural material may still be made by oxidizing species, such as O_2 , H_2O_2 , and OH , particularly at low concentrations of hydrogen, as will be articulated later in this review. Thus, numerical analysis shows that ignoring OH , but retaining H_2O_2 and O_2 , results in minimal error under normal PWR operating conditions, so that OH is generally not included in the list of electroactive species when calculating the ECP but, in any case, it is now included in the redefined $[H_2O_2^*]$. In the case of BWRs, the dominant electroactive radiolysis species are, unequivocally, H_2 , O_2 , and H_2O_2 , as noted above. Given the current proposals for the coolant chemistry in ITER, it is likely that the chemistry will fall somewhere between those of BWRs and PWRs; perhaps like that of a BWR operating on “Hydrogen Water Chemistry” (HWC), in which modest amounts of hydrogen (e.g., <1.0 ppm) are added to the feedwater to “suppress radiolysis” and hence to lower the ECP to values below the critical value for Intergranular Stress Corrosion Cracking (IGSCC) in sensitized austenitic stainless steels [2].

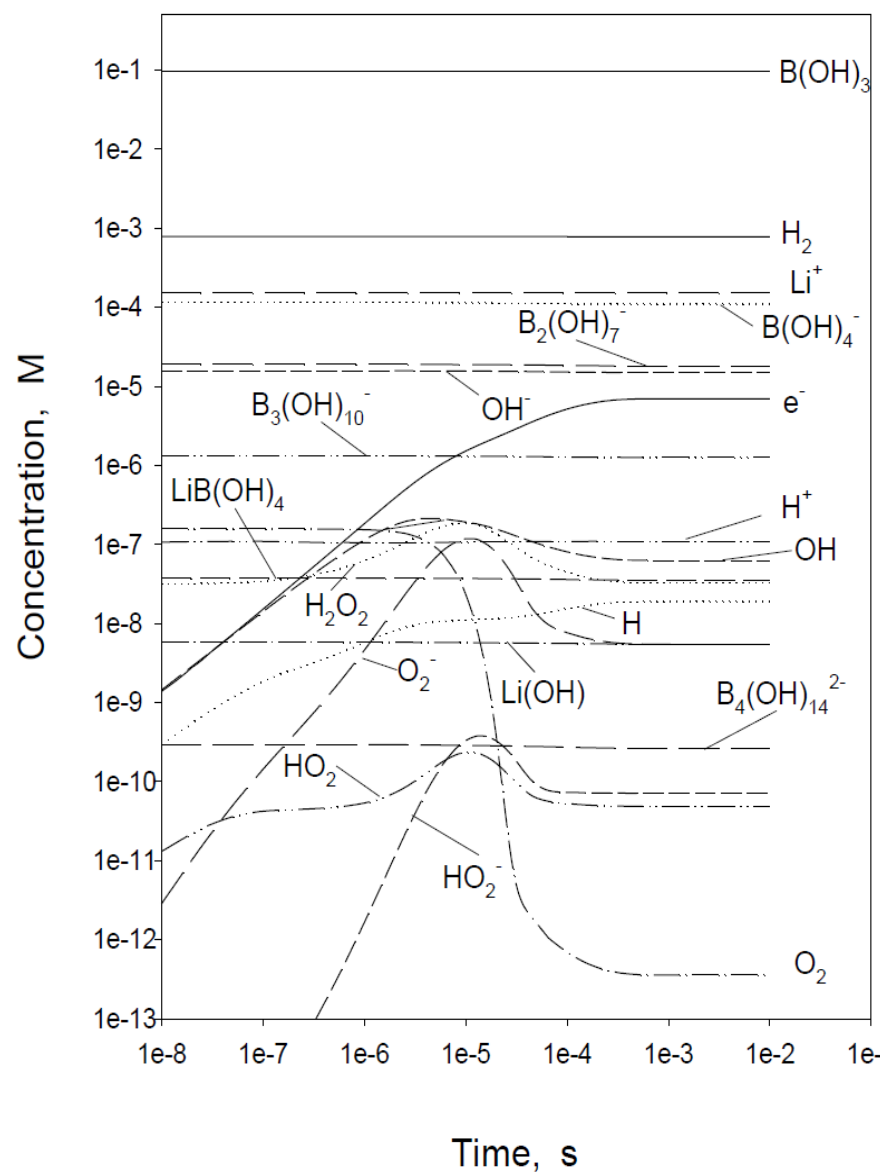


Figure 1. Concentrations of radiolysis and pH control species in the primary coolant of a PWR as a function of time towards achieving a local steady state for $C_{B,T} = 1500$ ppm, $C_{Li,T} = 1.5$ ppm, $T = 300$ °C, $[H_2] = 25$ cm³/kg STP (2.23 ppm), $\Gamma_n = 1 \times 10^{20}$ eV/cm³s, and $\Gamma_\gamma = 3 \times 10^{21}$ eV/cm³s. ©2017 OLI Systems, Inc.

2. A Brief Primer on the Physics and Technology of ITER

While this paper is not intended to be a review of ITER *per se*, it is necessary to provide some details of the device so that the impact of radiolysis on the operation of the IBED PHTS, in general, can be viewed in proper context. This background is especially important for those readers who are not conversant with thermonuclear physics. ITER is currently being constructed in Cadarache, France, and, as noted above, is intended to demonstrate the technical feasibility of fusion power by achieving $Q > 10$, where Q is the ratio of the output to input power. A thorough review of the physics of this technology is beyond the scope of this paper, so that only a brief discussion of the subject will be presented here. The reader is referred to the literature [1,3–32] for comprehensive descriptions of ITER and other fusion reactor concepts.

One great advantage afforded by fusion as an energy source is demonstrated in Table 1, which summarizes the mass conversions for five different energy production technologies. The conversion values are calculated using Einstein's energy/mass equivalence formula: $\Delta E = \Delta mc^2$, from the known energy yields, where ΔE is the energy produced upon conversion of a rest mass of Δm and c is the velocity of light (3×10^8 m/s). One sees from these data that the nuclear technologies—fission of $^{235}\text{U}_{92}$ and the fusion of deuterium and tritium—are by far the most efficient in converting mass into energy, except for particle/antiparticle annihilation (e.g., e^-p^+), for which the conversion efficiency is 100%. However, a cost-effective method for producing antiparticles (positrons) in sufficient amounts has yet to be devised to render this reaction to be of practical interest. It is also noted that of the technologies identified in Table 1, all but fusion and particle/antiparticle annihilation are currently contributing electrical energy to the national grid.

Table 1. Mass conversion factors for various energy production technologies.

Fuel	Energy (Kw-h)	Converted Mass (μg)	% Mass Conversion
1 bbl of oil	576	23	1.64×10^{-8}
1 ton of coal	2297	−92	0.92×10^{-8}
100 ft ³ of CH_4	12	−0.48	2.37×10^{-8}
1g of $^{235}\text{U}_{92}$		−929	0.093
Fusion of $^2\text{D}_1 + ^3\text{T}_1$		−0.019428 u	0.38
Annihilation e^-p^+	1.8219×10^{-31} u	− 1.8219×10^{-31} u	100

A second great advantage of fusion power is the limited amount of waste that is produced per unit of energy produced. Thus, according to an ORNL pamphlet, a small US city of 100,000 homes over 1 month requires 330,000,000 MJ of energy. If powered by coal, 150 railroad cars of bituminous coal are required that would produce 31,135 metric tons of CO_2 ; 31 metric tons of CO; 67 metric tons of NO_x ; 365 tons of SO_x ; 411 metric tons of particulates; and 33 kg of formaldehyde, in addition to about 22 lbs (10 kg) of U and 57.6 lbs (26 kg) of Th. On the other hand, a fusion reactor would consume 5 kg of D ($^2\text{H}_1$) and T ($^3\text{H}_1$) and produce 4 kg of helium ($^4\text{He}_2$), for which a market already exists. Clearly, from an environmental impact viewpoint, fusion is the preferred technology. However, the production of high-energy neutrons necessarily means that neutron activation and transformation of some elements in the structural materials will occur. Accordingly, a radioactive disposal problem upon decommissioning will be faced, not unlike that in the decommissioning of a fission reactor.

A schematic of the D–T fusion reaction, which has the lowest “ignition temperature” of alternative fission reactions listed in Table 2, is presented in Figure 2. It is seen that fusion is envisioned to occur via the fusion of the two nuclei to produce an unstable quasi-nucleus, comprising two protons and three neutrons. This entity then decomposes to produce a high-energy alpha particle ($^4\text{He}_2$, 3.5 MeV) and a high-energy neutron (^1_0n , 14.1 MeV) with a concomitant loss of mass, in addition to γ -photons of 15–25 MeV. For fusion to occur, the D and T nuclei must approach one another to within a few diameters of the nucleus (a few femtometers), where the strong nuclear force can overcome coulombic repulsion

and quantum mechanical tunneling of nucleons from one nucleus to the other can occur. This can only occur at very high kinetic energies that are sufficiently high that positively charged nuclei can approach one another to the requisite distance for tunneling to occur; that requires very high temperatures, of the order of 20 keV or more than 300,000,000 K. The energy released during the fusion process theoretically represents a 450:1 multiplication over the energy required to heat hydrogen nuclei to the fusion point [2].

Table 2. Mass conversion factors for fusion reactions between various isotopes of hydrogen.

Reaction	Reaction Equation	Initial Mass (u)	Mass Change (u)	% Mass Change
D–D	$^2\text{D}_1 + ^2\text{D}_1 \rightarrow ^3\text{He}_2 + ^1\text{n}_0$	4.027106424	-2.44152×10^{-3}	0.06062
D–D	$^2\text{D}_1 + ^2\text{D}_1 \rightarrow ^3\text{H}_1 + ^1\text{p}_1$	4.027106424	-3.780754×10^{-3}	0.09388
D–T	$^2\text{D}_1 + ^3\text{T}_1 \rightarrow ^4\text{He}_2 + ^1\text{n}_0$	5.029602412	-0.019427508	0.3863

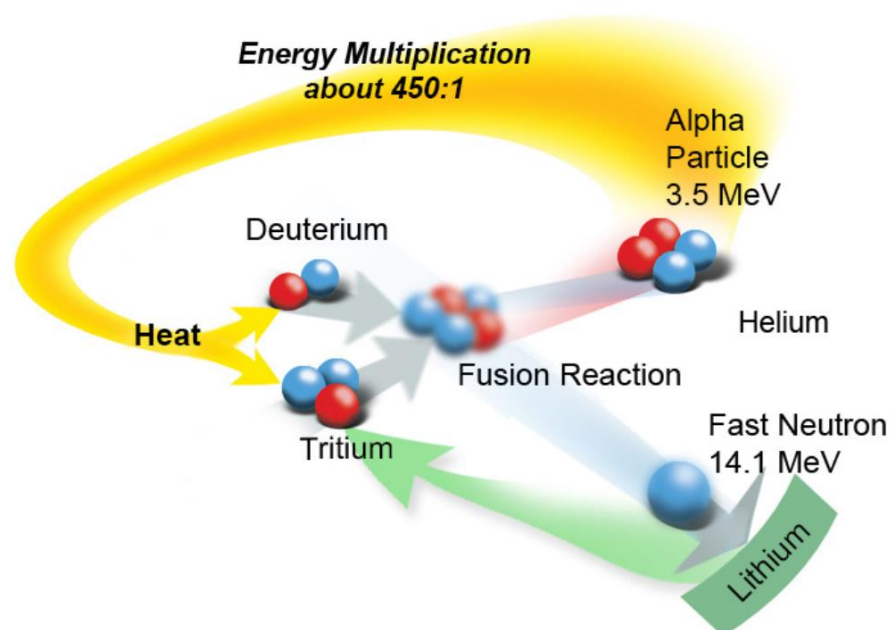


Figure 2. Schematic of the D–T fusion reaction. ©2018 US ITER.

Attempts to harness fusion power have been underway since the 1950s, during which two basic approaches have evolved. The first, toroidal magnetic confinement fusion (MCF), is a Russian invention in which a low-density D–T plasma is confined magnetically in a toroidal chamber and is heated to fusion temperatures using extremely-high-density current and high-energy neutral particle and/or ion injection. In the second approach, inertial confinement fusion (ICF), or laser implosion, a mixture of D–T is contained within a small pellet, which is pulse irradiated from all sides using high-energy lasers, with the resulting adiabatic compression raising the temperature to the fusion threshold. Thus, these two fusion devices attempt to emulate the processes that power the sun and the stars—viz. the fusion of deuterium ($^2\text{H}_1$) and tritium ($^3\text{H}_1$): $^2\text{H}_1 + ^3\text{H}_1 \rightarrow ^4\text{He}_2$ (3.5 MeV) + $^1\text{n}_0$ (14.1 MeV), as noted above, and that occur in thermonuclear weapons, respectively. However, several other fusion reactions involving the isotopes of hydrogen, as summarized in Table 2, are also possible. As noted above, the D–T reaction has the lowest “ignition temperature”, and hence this reaction is of the greatest interest in current fusion technology. It is also the reaction that results in the greatest conversion of mass into energy. Because this case uses tritium, which is not naturally occurring, tritium must be “bred” from some other nucleus, such as that described by the reaction $^7\text{Li}_3(^1\text{n}_0, ^4\text{He}_2)^3\text{H}_1$. On the other hand, if the D–D reaction was chosen, D is of plentiful supply in nature, as about 140 ppm of this isotope exists in natural water and the technology for its extraction is well developed.

However, it requires a higher ignition temperature, and the mass conversion factor is not as attractive as the D–T reaction.

In 1957, Lawson [6] derived the conditions that must be attained in the plasma for “breakeven” fusion (i.e., energy produced by fusion exceeding the energy input) as the “triple product”:

$$nT\tau_E \geq 3 \times 10^{21} \text{ keV} \cdot \text{s/m}^3 \quad (1)$$

where n is the plasma density ($\#/m^3$), T is the temperature (keV), and τ_E is the confinement time. The two approaches to controlled thermonuclear fusion differ in how these parameters are combined to achieve the Lawson energy balance. Thus, MCF aims at moderate n and T and a high τ_E to achieve the balance, while ICF makes use of high n and T combined with short τ_E to achieve the required breakeven condition. Furthermore, MCF seeks to produce a controlled, sustained “burn,” while ICF seeks to produce repetitive, miniature thermonuclear explosions. To date, MCF has come closest to attaining its stated goal.

ITER is an example of the first approach (MCF) and is the logical extension of JET (Joint European Torus), which is operated in Oxford, England, UK. JET achieved a Q -value (i.e., energy produced from fusion/input energy to heat the plasma) of 0.67 (16 MW out for 24 MW in), but ITER is expected to yield $Q \geq 10$ (500 MW out for 50 MW in) over a sustained “burn” of about 550 s followed by a dwell period of 1250 s, to yield a repetition period of 1800 s (Table 3). Thus, ITER is a confined plasma device comprising a toroidal vacuum chamber and 5.3 T, Nb₃Sn superconducting magnets that are designed to confine the hot plasma away from the walls.

Table 3. ITER Tokamak operating parameters (from ITER Technical Basis [4]).

Total Fusion Power	500 MW (700 MW)
Q -fusion power/additional heating power	≥ 10
Average 14 MeV neutron wall loading	0.57 MW m ⁻² (0.8 MW m ⁻²)
Plasma inductive burn time	≥ 400 s (550 s, including ramp-up and ramp-down).
Plasma major radius (R)	6.2 m
Plasma minor radius (a)	2.0 m
Plasma current (I_p)	15 MA (17 MA ^a)
Vertical elongation @95% flux surface/separatrix (k_{95})	1.70/1.85
Triangularity @95% flux surface/separatrix (δ_{95})	0.33/0.49
Safety factor @95% flux surface (q_{95})	3.0
Toroidal field @6.2 m radius (B_T)	5.3 T
Plasma volume	837 m ³
Plasma surface	678 m ²
Installed auxiliary heating/current drive power	73 MW ^b

^a The machine can operate at a plasma current of up to 17 MA, with the corresponding parameters shown in parentheses, but with limitations on other parameters (e.g., pulse length). ^b In subsequent phases of operation, a total plasma heating power of up to 110 MW may be installed.

Figure 3 provides a schematic layout of ITER’s Tokamak building, with the scale being indicated at the bottom of the figure. The Tokamak, itself, is located within a reinforced concrete building. The effluent of greatest concern is tritium (${}^3\text{H}_1 \rightarrow {}^3\text{He}_2^+ + {}^0\text{e}_{-1}^- + \bar{\nu}_e$, $t_{1/2} = 12.32$ years, $E = 18.6$ keV) because it readily diffuses through steel pipe walls. Accordingly, tritium must be removed by various scrubbing devices. Moreover, ${}^{16}\text{N}_7$ and ${}^{17}\text{N}_7$, which are produced by the nuclear reactions ${}^{16}\text{O}_8({}^1\text{n}_0, {}^1\text{p}_1){}^{16}\text{N}_7$ and ${}^{17}\text{O}_8({}^1\text{n}_0, {}^1\text{p}_1){}^{17}\text{N}_7$, respectively, are a potential radiological contamination issue. Both are radioactive (${}^{16}\text{N}_7 \rightarrow {}^{16}\text{O}_8 + \beta + \gamma$ and ${}^{17}\text{N}_7 \rightarrow {}^{17}\text{O}_8 + \beta + \bar{\nu}_e$) and will be produced in the radiation zone. They will then be carried by the coolant to non-irradiated regions of the PHTS, where they will establish γ fields that will contribute to the main REM cost of operation, like that of a BWR operating on Hydrogen Water Chemistry (HWC). One critically important engineering consideration is the need for great rigidity of the tokamak structure, particularly the coils because they are subjected to high Lorentz forces produced by the circulating plasma in the magnetic

field. Any distortion of the structure could affect the shape and stability of the plasma. Additional details on the structure of the Tokamak and the reactor building and related matters are given in [1,3–31].

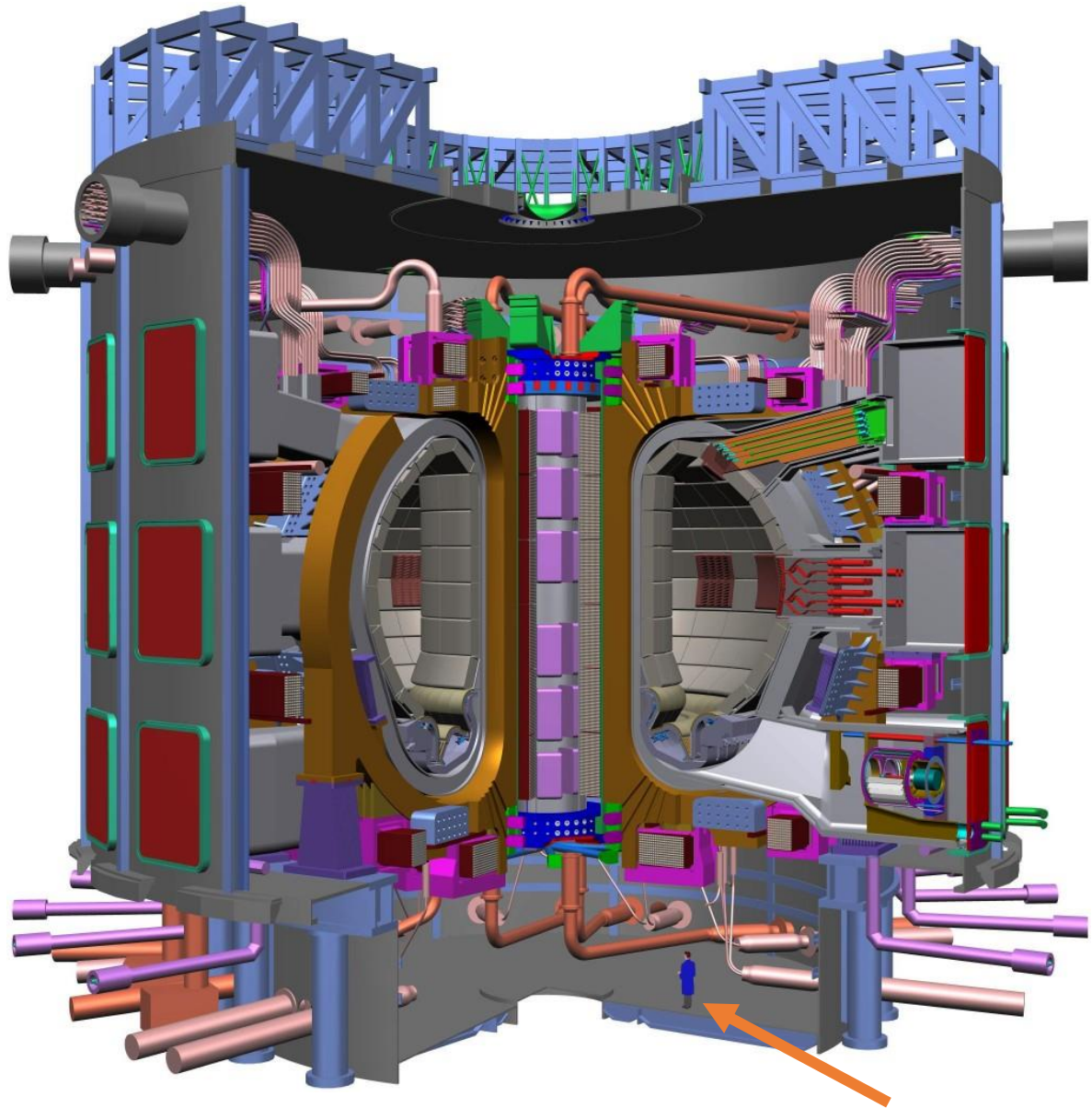


Figure 3. Cutaway view of the ITER fusion reactor (from ITER Technical Basis [4]). Note the size of the device in comparison with the human figure. ©2002 IAEA.

As noted above, the plasma is confined within the toroid by the magnetic field generated by the superconducting toroidal field (TF) coils and the central solenoid and is shaped by the six poloidal field (PF) coils (PF1 . . . PF6), which also protect the ports into the vacuum chamber, the blanket modules, the DIV cassette, and the control coils, as shown in Figure 4. The principal objective of this strong, shaped magnetic field is to keep the plasma away from the toroid walls. Since the plasma is at a temperature that corresponds well more than 300,000,000 K, no material, including beryllium, could withstand a “plasma strike”. Even if it did survive a transitory strike, the plasma would be contaminated that would interfere with the fusion process. Accordingly, the containment of the plasma is vitally important in magnetic confinement fusion technology.

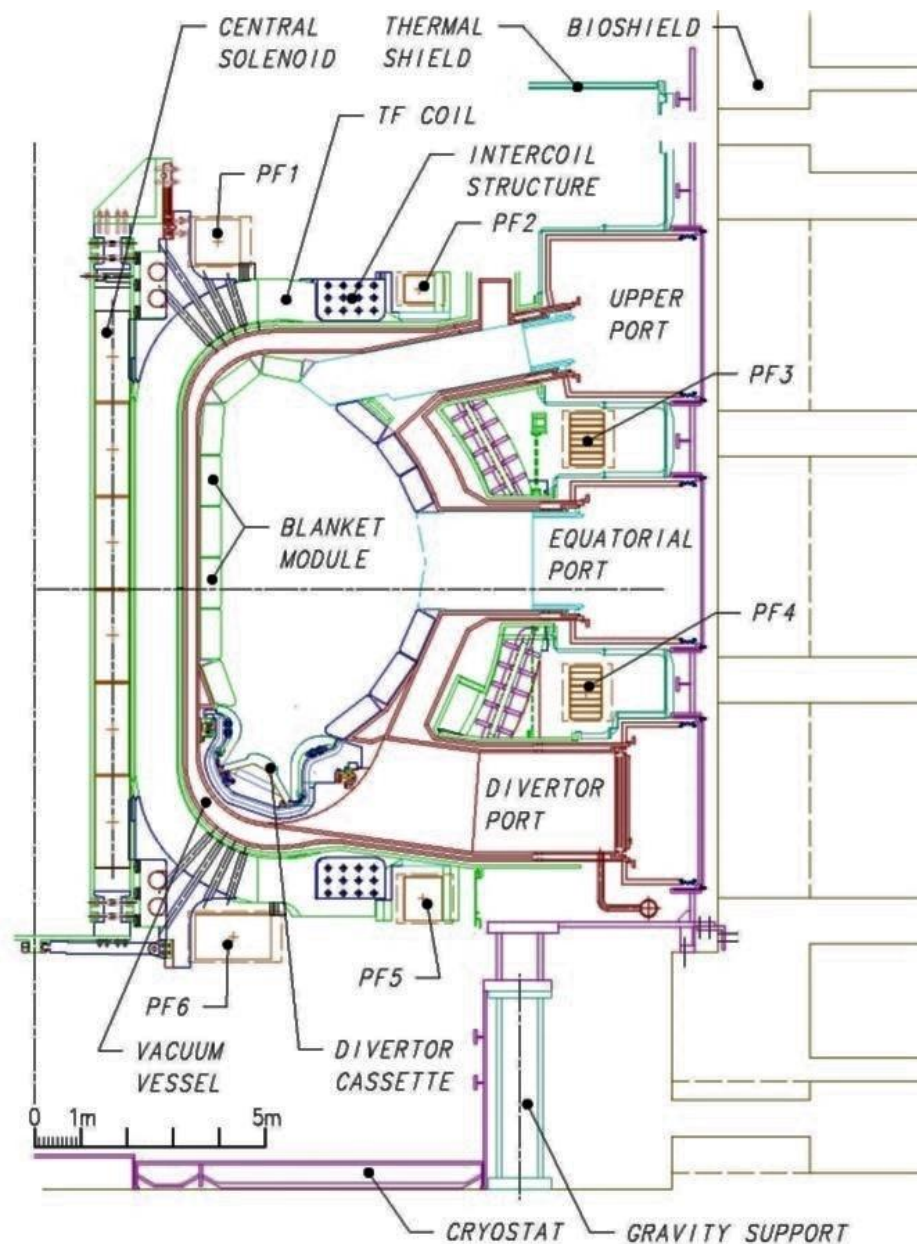


Figure 4. Vertical cross section of the ITER Tokamak. TF = toroidal field; PF = poloidal field. The six poloidal field coils that are used to shape the plasma are depicted as PF1, PF2, . . . , PF6 (from ITER Technical Basis [4]). ©2002 IAEA.

Figure 5 illustrates the spatial arrangement of the PF coils and error field correction coils in the ITER Tokamak. The error correction coils are used to correct for any imperfections in the magnetic field symmetry that is shaped by the TF and PF coils (Figures 4 and 5).

Table 3 summarizes the operating conditions envisioned for ITER. These are various design parameters and actual conditions that will be ascertained upon operation. Because the minimal Q value ($Q = 10$) is required for the demonstration of fusion power viability, the Q -value is particularly important. Anything short of this goal would require a major redesign of ITER and possibly development of an entirely new machine.

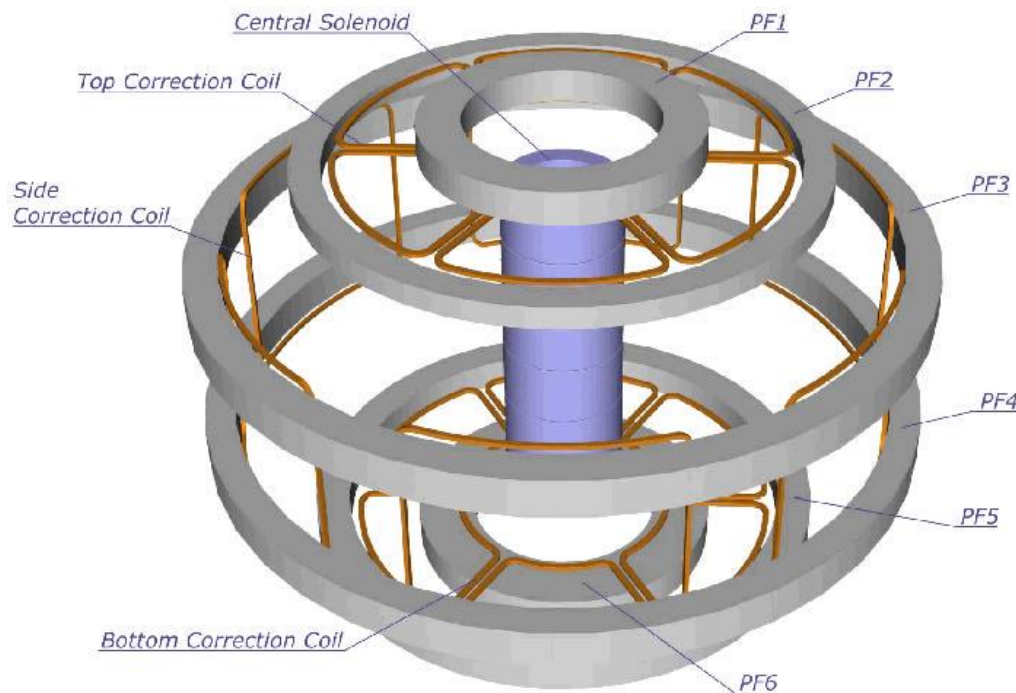


Figure 5. Correction coil arrangement in the ITER Tokamak (PF coils and error field correction coils (from ITER Technical Basis [4]). ©2002 IAEA.

Figure 6 provides the electron temperature, ion temperature, electron density, and helium density, and Figure 7 depicts the configuration of the plasma. Most important is the need to ensure that the extremely hot plasma does not contact the walls of the cavity because no material can withstand contact with the plasma without vaporizing. Preventing this contact is primarily the role of the six poloidal field coils (Figure 4), which also ensure plasma stability. The toroidal vacuum vessel is double-walled stainless steel and lined with Be-armored blanket modules, whose function is, amongst others, to breed tritium via ${}^6\text{Li}_3 + {}^1\text{n}_0 \rightarrow {}^3\text{H}_1 + {}^4\text{He}_2$ and to shield the vacuum vessel wall from errant instabilities of the plasma.

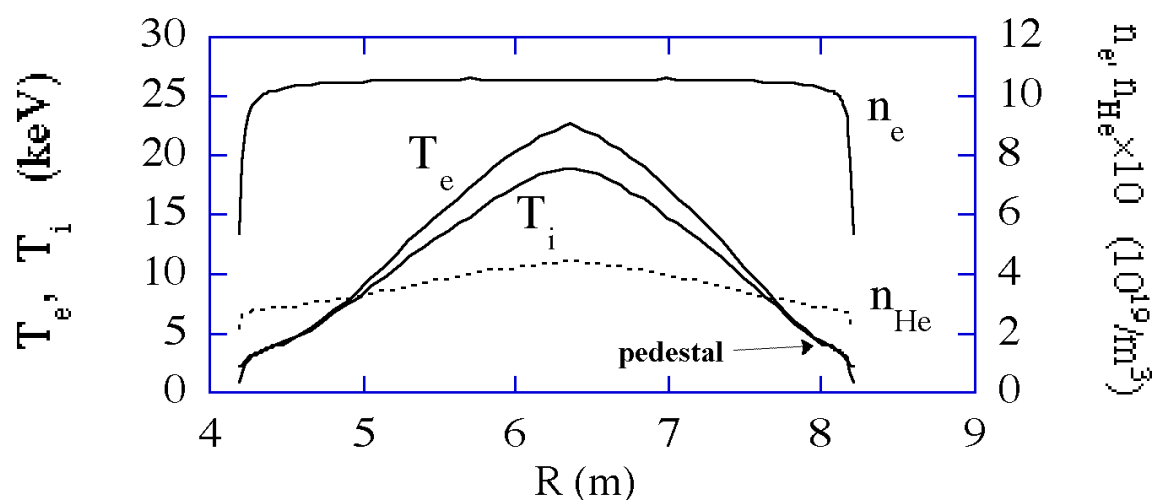


Figure 6. Profiles of electron temperature (T_e), ion temperature (T_i), electron density (n_e), and helium density (n_{He}) through the toroidal cavity (from ITER Technical Basis [4]). ©2002 IAEA.

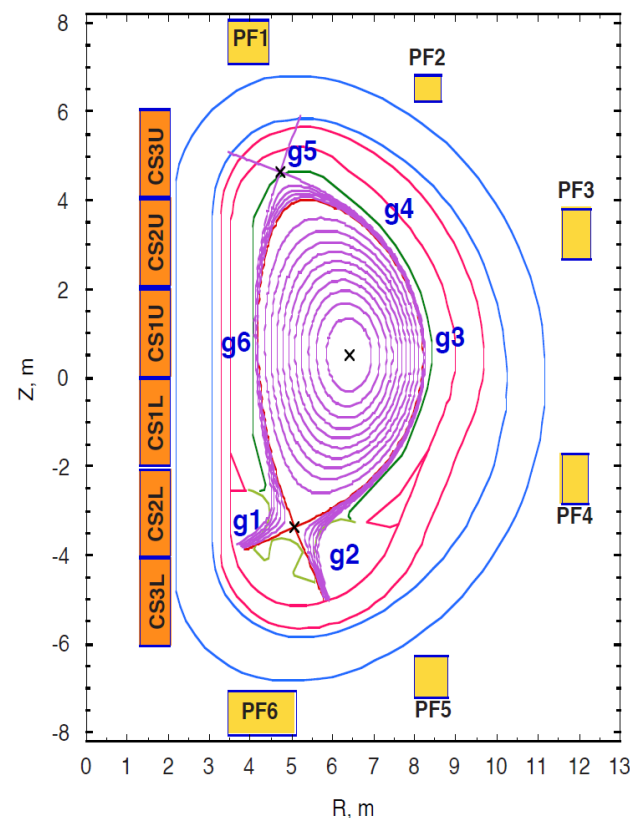


Figure 7. ITER nominal plasma configuration. The upper and lower “x” points are on different magnetic surfaces, defining two separatrixes, the primary one within the secondary one. The $g_1, g_2, \dots, g_6$ refer to gaps whose sizes are control variables for plasma stability. The six poloidal field coils that are used to shape the plasma are depicted as PF1, PF2, $\dots$, PF6 (from ITER Technical Basis [4]). ©2002 IAEA.

2.1. Tokamak Cooling Water System and Water Flow Configuration of the IBED PHTS

The TCWS, the primary cooling system of ITER, has a capacity to remove ~ 1 GW of heat from client systems and transfer the heat through the secondary cooling system to the environment. In addition, the TCWS provides baking services to plasma-facing components, draining, drying, and water chemistry control. To support these functions, the TCWS includes three PHTSs: IBED PHTS, Vacuum Vessel (VV) PHTS, Neutral Beam Injectors (NBI) PHTS; and three supporting systems: Draining System (DRS), Drying System (DRS), Chemical and Volume Control System (CVCS) [1,35]. A general view of TCWS is shown on Figure 8.

The largest and most complex loop of TCWS is IBED PHTS (shown with dark-blue colour in Figure 8), which is designed to remove 880 MW of heat from different in-vessel components. The IBED PHTS provides cooling water to the following components: First Wall/Blanket Modules; Test Blanket Modules, Divertor Cassettes; In-Vessel Coils; Diagnostics; and Plasma Heating Devices. It also provides water baking for in-vessel components and allows gas baking of the Divertor Cassettes [8,9]. The major components of the IBED PHTS include pumps, heat exchangers, baking heater, pressurizer, and pressure relief tank. Heat extracted from the IBED PHTS is rejected to the Heat Rejection System through the Component Cooling Water System loop.

The IBED PHTS chemistry is controlled by the CVCS, which includes mechanical filtration, ion exchange, and degassing [11,13]. It provides control of radiolysis and radiolytic products, among other functions. A small amount of coolant (roughly 1%) flows from the cold leg header through the CVCS loop and is returned to the hot leg header near the pressurizer.

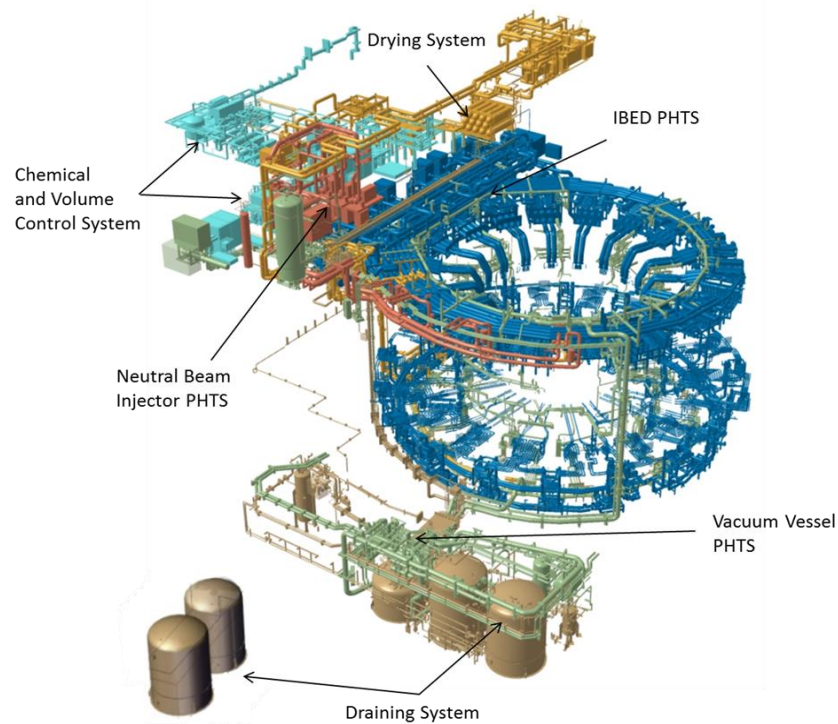


Figure 8. Tokamak Cooling Water System. General View [35].

The ITER will be operated in a pulse mode as depicted in Figure 9, with a ~550 s “burn” (which includes normalized ramp-up and ramp-down time), during which fusion occurs, followed by a 1250 s dwell. This 1800 s cycle is to be repeated during sustained operation. To minimize fatigue to the components, the number of inductive cycles during the lifetime of the ITER machine will be limited to 30,000. The initial plan for operating ITER and for the testing of the various components is shown in Figure 9 [4].

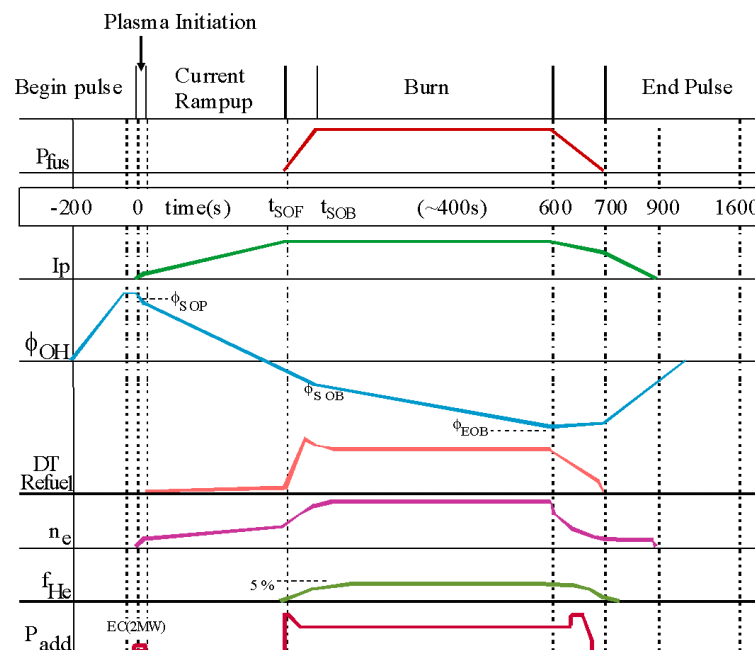


Figure 9. Standard plasma burn operation. P_{fus} = Fusion Power, P_{add} = Added power to initiate fusion, n_e = Electron density in the plasma, f_{He} = He density in the plasma, and I_p = Plasma current (from ITER Technical Basis [4]). ©2002 IAEA.

2.2. Radiation Dose Rates in the IBED PHTS

The production of high-energy neutrons and γ -photons by the fusion process is the cause of the radiolysis of water and the related corrosion issues in the heat transport system. The energy deposition values for neutron- and γ -irradiation for various IBED PHTS components are given in Ref. [4]. The energy dose rates for neutron irradiation are more than a factor of five higher than that for γ -photons, except in the port plugs where the ratio is predicted to be considerably lower and the dose rates themselves are predicted to be less.

2.3. Materials of Fabrication of the IBED PHTS

The materials scheduled to be used in the IBED PHTS are summarized in Figure 10. The materials are generally of three classes: austenitic stainless steels (e.g., XM-19, Types 316L and 316L(N) stainless steels), nickel-base corrosion-resistant alloys [e.g., Inconel (625)], and copper alloys (CuCrZr-IG) and pure copper. The stainless steels and nickel alloys are being chosen for their corrosion resistance and mechanical strength/stiffness, while the copper alloys are selected for their high thermal conductivity. A number of excellent publications are available on the materials challenges facing ITER designers [3,14–24,29,30,33,34,45,49], and it is expected that significant evolution in materials for specific applications will occur over the next two decades.

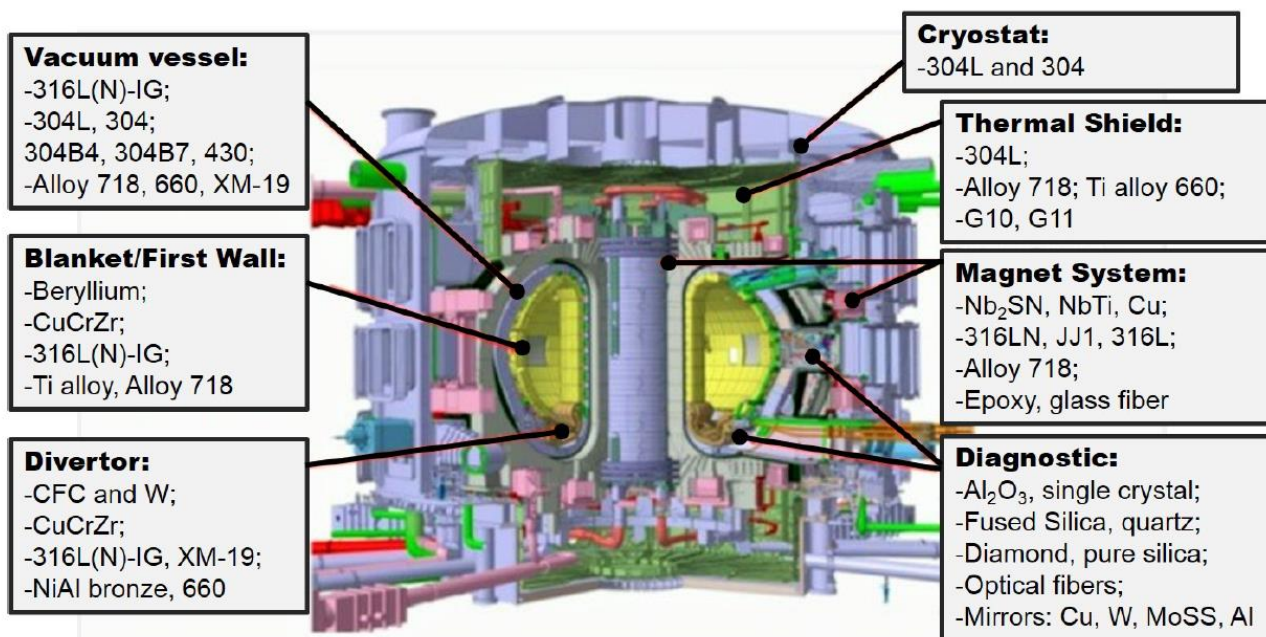


Figure 10. Summary of materials tentatively selected for ITER Tokamak [15]. ©2010 ITER Organization. This image is hereby used courtesy of the ITER Organization.

In any event, the alloys in contact with the coolant will corrode, albeit at different rates and in different forms (e.g., general corrosion, pitting corrosion, stress corrosion cracking, corrosion fatigue, crevice corrosion, erosion–corrosion, and hydrogen-induced cracking), depending upon the specific conditions that exist locally. These forms of corrosion are found in the primary heat transport circuits of water-cooled fission reactors and are expected to occur in water-cooled fusion reactors as well. Corrosion will result in the contamination of the cooling water with metal ions, including Cu^+ , Cu^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Cr^{2+} , and Cr^{3+} , along with their hydrolyzed derivatives, including oxide/hydroxide colloids, with the concentrations of each depending upon the exact conditions (e.g., redox potential, pH). Solid corrosion products in the form of CRUD (Chalk River Unidentified Deposits), as they occur in current fission reactors, are also expected and will be neutron irradiated

in the irradiation zone to produce radioactive isotopes (e.g., ^{60}Co) that will be deposited in out-of-core areas of the PHTS. This “activity transport” issue does not appear to have been thoroughly assessed, although its occurrence in the PHTS of fission reactors is well known. Although the neutron activated corrosion products (including dissolved ions) are not expected to significantly contribute to the radiolysis of water [28,37], they will contribute to the radiation fields in out-of-core areas that are not designed for the presence of such fields. Furthermore, the work of Yang et al. [26] shows that the formation of $^{16}\text{N}_7$ and $^{17}\text{N}_7$ will produce significant out-of-core radiation fields, in spite of the short half-lives of those isotopes (7.13 s and 4.173 s, respectively), not unlike a BWR operating on hydrogen water chemistry (HWC), in which the isotopes of nitrogen are transferred to the steam phase as NH_3 because of the net reducing conditions induced by the added hydrogen. Under normal water conditions, the coolant is oxidizing, and the nitrogen isotopes that exist in the liquid phase as the oxyanions of nitrogen (NO_2^- , NO_3^-), which are removed by the ion exchange columns. In the case of the ITER, where no boiling is contemplated, the isotopes will remain in the liquid phase, regardless of the redox conditions in the PHTS, but their removal will depend critically upon their chemical forms. In any event, contact dose rates of less than $700\text{ }\mu\text{Sv/h}$ upon shutdown for 1 h and $16.6\text{ }\mu\text{Sv/h}$ upon shutdown for 12 days after 20 years of operation are anticipated [26]. These dose rates may be compared with the allowable dose rate of ionizing radiation in the United States from terrestrial sources of about $0.04\text{ }\mu\text{Sv/h}$ (0.35 mSv/a) and are typical of those experienced by workers in the turbine hall of a typical BWR operating on hydrogen water chemistry.

The materials that have been selected for the all-important vacuum vessel (VV), because of its interface with the plasma, are also shown in Figure 10. The materials have been selected for four primary reasons:

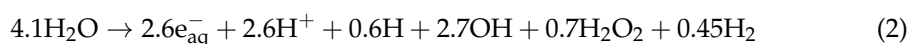
1. Resistance to the plasma. Thus, beryllium serves as an armor material for protection of IV components against the plasma. It is not in contact with the coolant water.
2. High thermal conductivity (Cu alloys).
3. Structural rigidity (stainless steels).
4. Corrosion resistance (nickel base alloys and stainless steels).

It is to be emphasized that the material choices should be dictated not only by their physical/mechanical attributes but also by their physico-electrochemical (e.g., corrosion) attributes, activation tendencies, and cost. Because few of the materials meet all the desired requirements, new materials are continually under active review and development [3,14–24,29,30,33,34,45,49].

3. Radiolysis of Water

3.1. Overview of Radiolysis of Water Issues

Upon the exposure of water and aqueous solutions of moderate concentration ($<1\text{ M}$) to ionizing radiation (i.e., electrons, neutron, gamma, alpha, and heavy ion), the energy is absorbed by the water to generate radiolysis products [36–208], which has been described by the overall reaction:



where the numbers are the time-dependent, radiolytic yields (i.e., G-values, number of molecules produced per 100 eV of absorbed energy). Note that the above stoichiometric reaction is both mass and charge balanced and any mechanism that is proposed for the radiolysis of water should result in the same balances, but it is not evident that that is always the case (see below). The G-values may be converted to SI units (mol/J) by multiplying the number of molecules produced per 100 eV of absorbed energy by 1.036×10^{-7} . An enormous literature exists on the radiolysis of water [36–202], and a comprehensive review of the work is beyond the scope of the current paper. Instead, the reader is referred to various monographs and reviews on the subject [36–43,67,68,73,79,81,121,122,158]. Here,

we discuss only those aspects of the subject that are relevant to reactor (fission and fusion) heat transport systems (HTS).

The radiolysis of water in water-cooled nuclear (fission) reactor (WCNR) primary heat transport circuits has long been recognized as a potential source of corrosive, oxidizing species, such as O_2 , H_2O_2 , and OH , and for this reason hydrogen is added to PWR primary coolant circuits [168,205,248,249,252,253,265–269] and, in more recent years, to BWR coolant circuits. The hydrogen addition is made to suppress the radiolytic generation of oxidizing species and/or to displace the corrosion potential of structural components in the coolant circuits in the negative direction. This has been accomplished in the case of PWR primary coolant by adding large amounts of hydrogen to the coolant [20–70 cc(STP)/kg, 8.93×10^{-4} – 3.13×10^{-3} m, 1.8–6.3 ppm], seemingly with the philosophy that “if a little is good, a lot more must be better.” It is argued elsewhere [249,266] that a “lot more” is definitely “not better” regarding the integrity of Alloy 600, which is used extensively in PWR steam generators as tubing material. In the case of BWRs, the IGSCC of sensitized Type 304SS primary coolant components—particularly the recirculation piping system, but more recently in IV (in-vessel) components—has been attributed to an excessively high ECP resulting from the generation of oxidizing species (i.e., O_2 and H_2O_2 due to the radiolysis of water), and to a sensitized microstructure that results from either thermal sensitization or neutron irradiation-induced grain boundary segregation (i.e., sensitization) above a certain fluence (i.e., accumulated dose $> 10^{21}$ n/cm², energy > 1 MeV) [33]. The nuclear fission power reactor community only slowly accepted the ECP as the prime parameter in determining the accumulation of corrosion damage, possibly because electrochemistry is seldom, if ever, included in the Mechanical and Nuclear Engineering curricula at universities that form the basis of a nuclear engineering degree. The impact that ECP has on CGR is roughly exponential if the ECP is above a critical potential for IGSCC (E_{IGSCC}) [106,208,218–237,250,257,260–264,281–289], although the rate also depends upon the stress intensity factor, the extent of cold-working of the substrate, the conductivity of the environment, and the flow velocity of the coolant across the surface. Below this critical potential, the CGR is determined by mechanical creep that does not pose a threat to reactor integrity. Because fusion reactors, including ITER, employ water as the primary coolant, these same factors are expected to be issues in the development of nuclear fusion power technology, and it is of the utmost importance that the fusion community benefit from the lessons learned in the fission community.

Figure 11 depicts the initial events that are envisioned to occur in aqueous solutions upon the absorption of energy from ionizing radiation, such as γ -photon, electron, neutron, α -particle (4He_2), and heavy ion (e.g., C^{6+}), etc. [37]. These events are considered to occur in three stages: (1) the “physical” stage, in which ionization occurs ($< 10^{-15}$ s); (2) the “physico-chemical” stage, in which reactions occur within the spurs to form the primary products (10^{-15} – 10^{-12} s); and (3) the “chemical stage” ($> 10^{-12}$), in which the species escape from the spurs to react amongst themselves in the bulk coolant. Although there is considerable disagreement as to the periods over which these stages occur [36], there does seem to be agreement that the species that leave the spurs constitute the “primary species,” whether it be 10^{-12} s or 10^{-9} s after the initial ionization event. Within the vibrational time of a chemical bond (10^{-16} – 10^{-12} s), the water molecule is envisioned to ionize and dissociate to form a variety of elementary products, including H_2O^+ , e_{aq}^- , OH , and H_3O^+ , as depicted in Figure 11. Table 4 summarizes the reactions that are envisioned to occur within the spurs as identified in a study by Buxton [67]. Note the absence of HO_2 , HO_2^- , O_2 , and O^- , implying that these species are considered to form via reactions that occur outside the spurs at longer times.

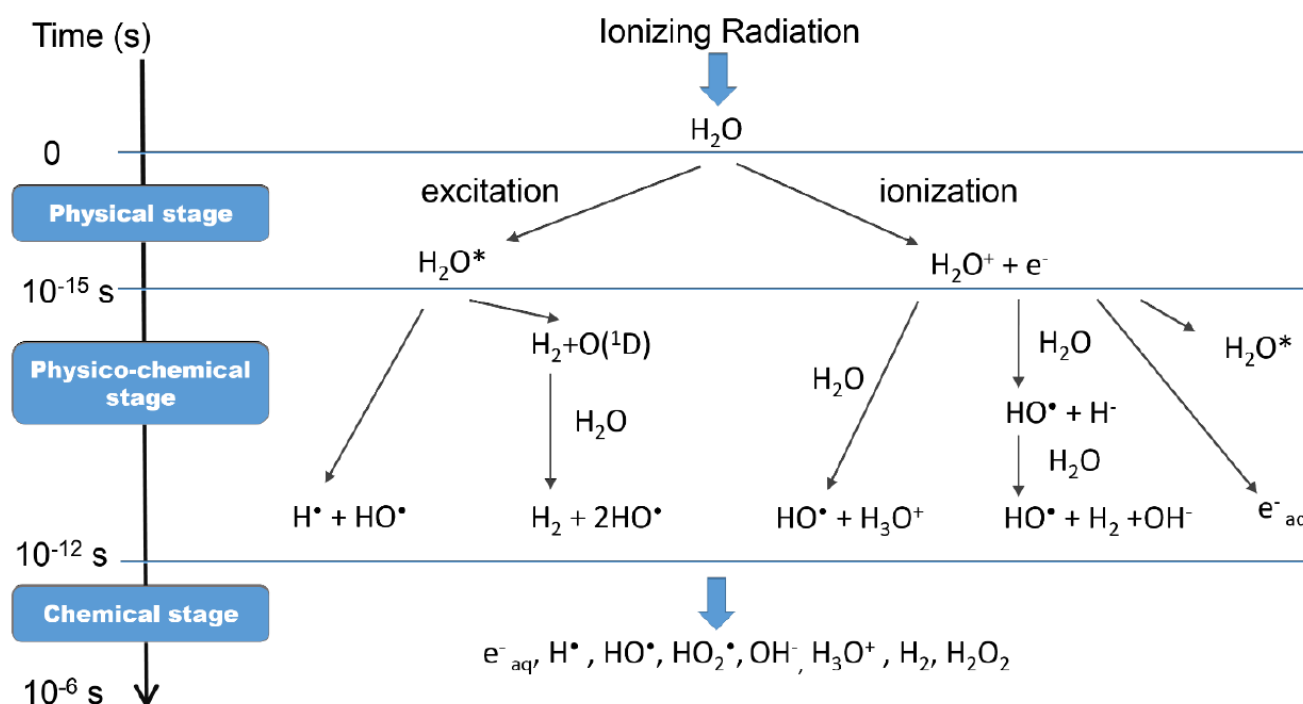


Figure 11. Envisioned sequence of initial events in the radiolysis of water. The superscript * indicates a radical species [37].

Table 4. Spur reactions in the radiolysis of water [67].

	Reaction	$10^{-10} \text{ k/dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
(1)	$\text{e}^-_{\text{aq}} + \text{e}^-_{\text{aq}} \rightarrow \text{H}_2 + 2\text{OH}^-$	0.54
(2)	$\text{e}^-_{\text{aq}} + \text{OH} \rightarrow \text{OH}^-$	3.0
(3)	$\text{e}^-_{\text{aq}} + \text{H}_3\text{O}^+ \rightarrow \text{H} + \text{H}_2\text{O}$	2.3
(4)	$\text{e}^-_{\text{aq}} + \text{H} \rightarrow \text{H}_2 + \text{OH}^-$	2.5
(5)	$\text{H} + \text{H} \rightarrow \text{H}_2$	1.3
(6)	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	0.53
(7)	$\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$	3.2
(8)	$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$	14.3

During the physico-chemical stage (10^{-15} to 10^{-12} s), the diffusion length of these products (x) can be estimated from $x \sim \sqrt{Dt}$, where D is the diffusivity (taken as 10^{-4} cm²/s for e_{aq}^- , H, and OH) to be approximately 10^{-8} cm (0.1 nm), which is of the same order as the diameter of a water molecule. At longer times (10^{-12} to 10^{-7} s), the fragments react among themselves to form molecular products, including H₂O₂, and H₂ within the spurs, according to Buxton [67]. During this stage, the diffusion length is estimated to be about 10 nm, suggesting that some of the species will have moved out of the spurs. Assuming a spur width of 1 nm, it is evident that the primary yields should be taken from pulse radiolysis studies with pulse lengths of no more than 1 ns. At still longer times ($>10^{-7}$ s), these, and the remaining elementary products (i.e., e_{aq}^- , H, OH, O, and H₃O⁺), diffuse from the spurs into the bulk environment and continue to react at times up to about 0.1 s, when steady state is predicted to be achieved (see Figure 1). It is important to differentiate between the primary products that are formed within the spurs and the products that form in the bulk environment via reactions involving primary products that diffuse from the spurs, or that are produced by the reactions that occur in the bulk at times more than 10^{-7} s. The first group is termed the “primary products,” whereas the second group is known as “secondary products.” The distinction is important because a radiolysis model comprises a radiolytic source term that describes the formation of the primary products at

essentially zero time, and a set of reactions that account for the formation of the secondary products as the system proceeds toward a steady state. For this reason, it is important to use “primary radiolytic yields” (i.e., G-values), which are expressed in units such as number of molecules/100 eV absorbed or the preferred SI equivalent (mol/J), corresponding to times of less than ~1 ns (Figure 12) in the source term. It is important to note that the yield of elementary products continues to evolve within the spurs due to various reactions (Table 4), as is shown in Figure 12 [67].

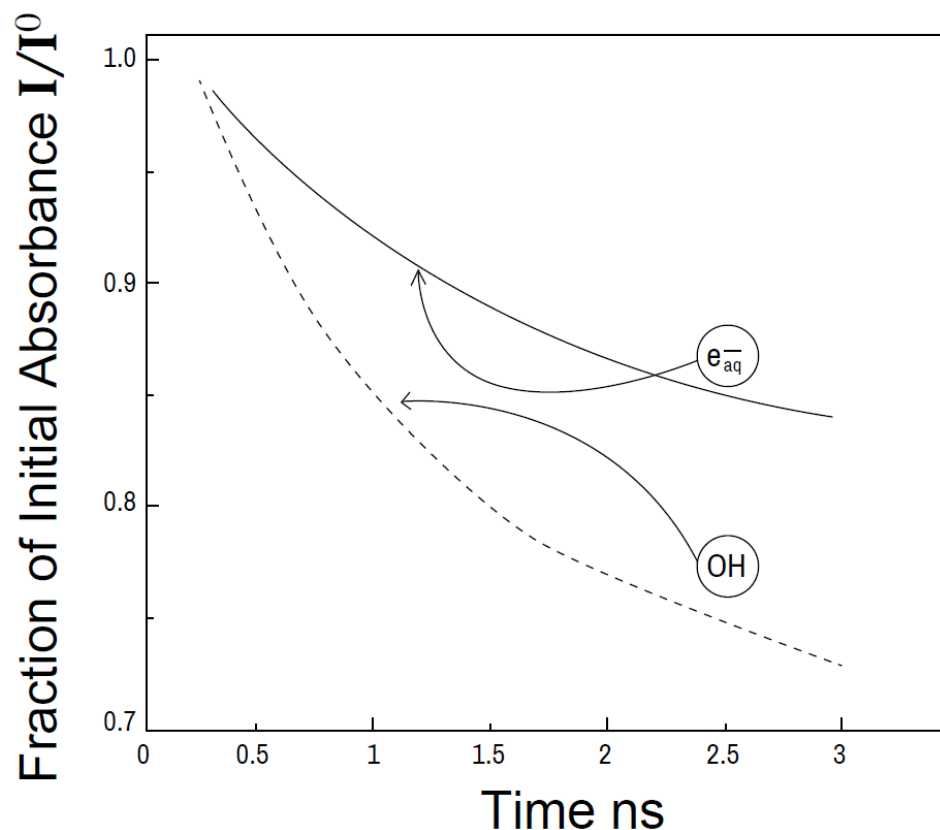


Figure 12. Decay of the concentrations of aquated electrons (e_{aq}^-) and OH radical generated by a 30 ps pulse of 20 MeV electrons in liquid water. Adapted from [67].

The yield of the primary products decreases sharply with time over a period of a few nanoseconds, which can be attributed to the products reacting amongst themselves within as well as external to the spurs. Formation of the secondary products results from the chemical reactions outside the spurs (Table 4) and at longer times than those shown in Figure 12, thereby emphasizing the need for truly “primary” yields. Clearly, if quasi-steady-state yields are used in the model, the impact of the chemical reactions will have been counted twice. It is not evident upon review of various models whether this issue is widely recognized or has been addressed. It is evident from the above discussion that no clear demarcation exists between the “primary” and the “secondary products in the radiolysis of water, except to note that practical definition of the primary products defines them as being those products that are formed at the shortest possible times (<1 ns).

As noted above, the ECP is the key parameter in describing the susceptibility of reactor coolant components to corrosion damage. Experience has shown that the direct measurement of ECP in fission reactor coolant circuits at appropriate locations is very difficult [260] because of the harsh conditions under which the measurements must be made, and the same difficulties are expected to be experienced in operational fusion plants. The major challenge for in-reactor ECP measurements has been to devise a reference electrode that can withstand the harsh environmental conditions that exist within a reactor pressure vessel (RPV) for any useful amount of time. Because of the lower operating

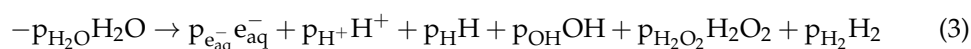
temperature of the ITER IBED PHTS (100 °C–150 °C) compared with those that exist in a BWR (288 °C) or a PWR (290 °C to 330 °C), in situ electrochemical monitoring of corrosion in the PHTS in ITER is expected to be feasible and should be encouraged to avoid many of the corrosion problems that have plagued fission light water reactors. A trend in recent years involves using platinum as a reference electrode because it is simple and rugged. However, a platinum electrode is an indicator electrode, whose potential is a function of the redox conditions; that is, a function of the very property that one is trying to sense. This is particularly problematic when measuring the ECP in the primary coolant circuit of a BWR, including BWRs operating on HWC. In the case of a PWR operating with a sufficiently high hydrogen concentration, a platinum electrode adopts the hydrogen electrode reaction (HER) equilibrium potential, and the reference electrode potential may be converted to the standard hydrogen electrode scale by knowing the partial pressure of hydrogen and the pH of the coolant.

Electrochemists will recognize that the ECP is a mixed potential, the value of which is determined by the balance of the partial currents involving oxidizing and reducing species in the environment and the kinetics of dissolution (i.e., corrosion) of the substrate [216]. To calculate the ECP, then, it is important, in principle, that the concentrations of all radiolytic species be determined because these species are electroactive, as noted above. However, as noted above, theory shows that the contribution that any given species makes to the ECP is determined primarily by its concentration, as noted previously, so that only the most prevalent electroactive species in the system determine the ECP [216]. This is a fortunate finding, at least in the case of BWRs, because the various radiolysis models for calculating species concentrations do not determine the concentrations of the minor species accurately, nor are there available electrochemical kinetic data for these species. In the case of PWRs, however, model calculations (e.g., Figure 1) indicate that H, OH, and possibly e_{aq}^- are also important species in addition to H_2 , and this may be true for ITER as well. However, as noted previously, this difficulty may be overcome to a significant extent by defining the new concentrations $[O_2^*] = [O_2] + 0.5[O]$, $[H_2O_2^*] = [H_2O_2] + 0.5[OH]$, and $[H_2^*] = [H_2] + 0.5[H] + 0.5[e_{aq}^-]$, where the concentrations of the species on the right side are those predicted by the radiolysis model, and those on the left side are the concentrations that are used in the mixed potential model (MPM) [216] for calculating the ECP and in the Coupled Environment Fracture Model (CEFM) [224] for calculating the CGR. This strategy avoids the problem of not having access to electrochemical kinetic data (e.g., exchange current densities, reaction orders, transfer coefficients) for the redox reactions involving H, OH, HO_2 , O_2^- , and e_{aq}^- that are of interest, by noting that the transport of these species to the metal surface and hence the associated partial current densities are mass transport controlled and are not sensitive to the kinetic parameters for the charge transfer processes at the interface.

To calculate the species concentrations, the combined effects of the primary radiolytic yield of each species due to the absorption of ionizing radiation by water—and the changes in concentration due to chemical reactions and fluid convection—must be considered. This problem reduces to one of solving as many stiff, coupled, simultaneous first-order differential equations as there are species in the system (see [218,219]). One of the major problems involved in describing the radiolysis of water is deriving a physico-chemically viable reaction model to describe the radiolysis of water and devising efficient algorithms for solving the resulting equations.

Before analyzing the various proposed models, it is first necessary to define “reaction model.” A common definition is as follows [290]: “Chemical reaction models transform physical knowledge into a mathematical formulation, so that that knowledge can be utilized in computational simulation of practical problems”. This rather cumbersome, but appropriate, definition is replaced for the present purposes by the following, more refined definition: “A reaction mechanism is a collection of elementary reactions that describes the course of a reaction and that, when added together, yield the overall stoichiometric process”.

Each elementary reaction proceeds via a single transition state (i.e., activated complex) and cannot have a kinetic order greater than 2. Furthermore, upon adding the elementary reactions, the correct stoichiometric reaction should be obtained. The restriction on the kinetic order is often explained by drawing an analogy to the game of billiards. Thus, the collision of two balls is common (indeed, it is the purpose of the game), but the collision of three balls simultaneously has a vanishingly small probability as the period of the event is made smaller. If a reaction in the mechanism has a kinetic order greater than 2, it is commonly referred as being a “non-elementary reaction” and can be broken down into a more fundamental set of bimolecular or unimolecular (i.e., elementary) reactions. This will be illustrated later with specific reference to the radiolysis of water. Thus, as noted above, an important theoretical property of an elementary reaction is that it passes through a single activated complex (transition state) along the reaction coordinate (i.e., that path from the reactants to products). Furthermore, in condensed, ionizing media, such as water, the reactions between species of like charge (i.e., anion–anion or cation–cation reactions) are generally excluded because coulombic repulsion prevents the ions from approaching each other closely enough for bond formation or particle (e.g., electron) exchange to occur, except in the case of outer-sphere charge (electron) transfer reactions of the form A^m/A^n , where $m = n \pm 1$ [273]. Note that in these reactions, the element (A) remains unchanged (i.e., is the same on both sides of the reaction); only the charge on each species is affected due to electron transfer. They are termed “outer sphere” reactions because the hydration sheaths keep the reaction centers sufficiently well-separated that coulombic repulsion can be overcome at ambient temperature, but the centers are sufficiently close that charge transfer via quantum-mechanical tunneling can occur. These criteria will be used to judge the veracity of a radiolysis model. Thus, according to Buxton’s criterion (Table 4 [67]), the first reaction (the “source reaction”) in the model should read:



where the p -values are the primary yields that are measured under pulse radiolysis conditions at sub-nanosecond time scales. The sum of this reaction and the reactions in the model should yield the stoichiometric reaction for the decomposition of water, which for a sufficiently long time can be written as



where the s -values are the steady-state yields that would be observed, for example upon continuous radiolysis over a sufficiently long time that the concentrations of all species came to a steady-state (see Figure 1, for example). If irradiation ceases, the radicals recombine such that after an extended period, the stoichiometric reaction becomes $\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2\text{O}_2$, assuming that no recombination between H_2 and O_2 does not occur at the low concentrations of these species in aqueous solution.

3.2. Past Radiolysis Modeling of Fission Reactor Coolant Circuits

For the most part, the models previously employed for modeling water radiolysis in the primary coolant circuits of water-cooled nuclear fission power reactors, including BWRs and PWRs, can be traced back to original work of Burns et al. conducted in the 1970s [44]. While a complete review of all models is not possible, because of limited space and limited access to all the pertinent, nonpublished literature, several important issues have been identified. The various issues identified and that must be addressed in future work are summarized as follows:

Reactions appear to have been added to, or subtracted from, previous models to later ones in an ad hoc manner without consideration of mathematical or chemical constraints that must be met. Because these models are massively undetermined in a mathematical sense (i.e., there are many more unknown parameters than there are observations), many re-

actions can be added or removed with little impact on the predicted species concentrations, as revealed by a sensitivity analysis [292].

Many models contain > 40 reactions, each of which is characterized by two parameters: the rate constant and the activation energy. If these parameters were determined by mathematical optimization, one would need at least twice the number of experimental observations (i.e., >80), some of which (e.g., two per reaction) would need to be at different temperatures to establish the activation energies. Because the radiolysis products are highly energetic (e.g., H, OH, e_{aq}^-), many models tacitly assume that the reactions involving these species are diffusion controlled and hence that the rate constants can be calculated from chemical kinetic theory [132]. Once this is accepted, the activation energy is set to 12.6 kJ/mol, which is typical for diffusion-controlled processes. For other reactions, there are directly measured values for the rate constants and activation energies (e.g., for the reaction $H_2O_2 \rightarrow H_2O + 1/2O_2$). Even so, the number of unknowns in the models generally far exceeds the number of independent experimental observations, rendering the models massively underdetermined mathematically (again, there are many more unknown parameters than there are observations). The problem is further compounded by noting that, in most cases, it is not possible to determine exactly what is contained within the experimental database because any calibrating data are seldom reported, with some notable exceptions (e.g., [59]). Accordingly, it is a mistake, in the authors' opinion, to regard these "models" as physico-chemical "mechanisms" in the conventional sense; instead, they should be regarded as being collections of reactions with "model-specific" parameter values that predict the concentrations of the dominant radiolysis products (O_2 , H_2 , H_2O_2) under specific conditions in specific systems (e.g., BWR primary coolant circuits). They lack the fundamental validity accorded by the laws of chemistry. As an example, in one of the author's own works [218], it was necessary to arbitrarily change the rate constant of the reaction $H_2O_2 \rightarrow H_2O + 1/2O_2$ to successfully predict the oxygen and hydrogen concentrations in the recirculation piping of BWRs, although the changes required in the rate constant were restricted to the range of values that had been reported in the literature for this reaction [91,97,210–214]. The success of this procedure can probably be attributed to the fact that the above reaction involves two of the three dominant radiolysis products, H_2 , O_2 , and H_2O_2 . However, once calibrated, the model does successfully account for the spectrum of radiolysis behavior in many BWRs worldwide. The reader should also note that the excessive number of "elementary" reactions affords extreme flexibility, and this undoubtedly contributes to the success of the models.

A third major issue concerns the radiolytic yields (G-values), which are defined as the number of species (e.g., atoms, molecules, ions) produced by the absorption of 100 eV of energy by the water or more fundamentally in SI units of mol/J. This issue was noted previously in this review, but its importance requires further analysis here. It is important to note that there exist two important definitions of the G-values. The first is for the processes that occur within the track (i.e., spur) of the ionizing radiation within a timeframe of 10^{-15} to 10^{-12} s, as depicted in Figure 11. In this case, only the ionization fragments of the water molecule are produced (i.e., H, OH, O, e_{aq}^- , H^+ , OH^-) and some small amount of molecular products that form within the spurs during the "physico-chemical stage" (e.g., H_2 and H_2O_2 , see Table 4), because the time is too short to allow significant reaction between all the fragments. These are termed the "primary radiolytic species," and their formation is measured by the "primary radiolytic yields" as G_i^p = number per 100 eV of energy that is absorbed or in mol/J as measured at sub-nanosecond time scales. The bulk of the radiolysis products are formed or annihilated outside of the spurs over much longer timeframes (10^{-12} s to 10^{-1} s). The G-values for many of the primary radiolytic species can be measured using pulse radiolysis methods [47,48,51,58,67,69–71,86,109–112,115,118,124,125,130,135,139,145,148–150,169,170,173,174,177,178,180–183,194–203,210], including the more recently developed nanosecond to sub-nanosecond [71,150,173,174,178,197] pulse radiolysis techniques using both low and high LET (linear energy transfer) radiation, with the concentration of the radiolysis product being determined by absorption spectroscopy. Ex-

periments show that the apparent G-values for species such as OH decrease with time over time scales of a few nanoseconds (Figure 12). This decrease is attributed to reactions that consume OH within the spurs or within the physico-chemical stage (Table 4).

On the other hand, some G-values, particularly in earlier reports, appear to have been measured under steady-state or quasi-steady-state conditions, most commonly employing a continuous radiation source, such as a radioactive isotope (e.g., ^{60}Co), a reactor (e.g., neutrons), or an accelerator (e.g., protons, alpha particles, electrons). As shown from pulse radiolysis studies, the apparent G-values change substantially with time (e.g., Figure 12), so that the steady-state values are likely to be significantly different from those for the immediate (<100 ns) formation of the radiolysis products (i.e., the primary yields). Even though this issue has been known for many years, many models appear to employ steady-state G-values, rather than the primary values corresponding to the yields when the processes that occur within the spur are complete, after about 10^{-9} s [37,43]. This is an important issue because it has been shown that the radiolytic yields for various radiolysis products can have an important impact on the ECP in reactor primary coolant circuits [252].

Furthermore, summation of the left sides and right sides of the reactions listed in Table 4, after including the source reaction, allowing for cancellation of the same species occurring on both sides, generally does not yield the stoichiometric equation for the decomposition of water. It appears that all the models for the radiolytic decomposition of water reviewed here suffer from the same malady. It is important to re-emphasize that a “mechanism” or “model” is not simply a compilation of all possible reactions that may have been studied individually, as this lack of mass balance illustrates. In summary, most of the models that have been proposed for the radiolysis of water fail to be constrained by the well-established rules of chemistry and should be reformulated.

Upon reviewing the reactions compiled in Table 5 and in other models, it is apparent that several reactions are not viable because they are not elementary, they postulate reaction between species of like charge, they do not mass balance, or they do not charge balance. These reactions are compiled in Tables 6 and 7.

Table 5. Radiolysis model used by Macdonald et al. [216–244] to model the primary coolant chemistry of BWRs, with the rate constant of Reaction (30) being used as the “calibrating” parameter. All but Reaction (30) and its kinetic data come from Burns and Moore [44].

No.	Rate Constant (L/Mol-s)	Activation Energy (Kcal/Mol)	Chemical Reactions
1	1.6×10^1	3.0	$e_{aq}^- + \text{H}_2\text{O} = \text{H} + \text{OH}$
2	2.4×10^{10}	3.0	$e_{aq}^- + \text{H}^+ = \text{H}$
3	2.4×10^{10}	3.0	$e_{aq}^- + \text{OH} = \text{OH}$
4	1.3×10^{10}	3.0	$e_{aq}^- + \text{H}_2\text{O}_2 = \text{OH} + \text{OH}$
5	1.0×10^{10}	3.0	$\text{H} + \text{H} = \text{H}_2$
6	2.0×10^{10}	3.0	$e_{aq}^- + \text{HO}_2 = \text{HO}_2$
7	1.9×10^{10}	3.0	$e_{aq}^- + \text{O}_2 = \text{O}_2^-$
8	5.0×10^9	3.0	$2e_{aq}^- + 2\text{H}_2\text{O} = 2\text{OH}^- + \text{H}_2$
9	4.5×10^9	3.0	$\text{OH} + \text{OH} = \text{H}_2\text{O}_2$
10	1.2×10^{10}	3.0	$\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$
11	1.2×10^{10}	3.0	$\text{OH} + \text{O}_2^- = \text{OH}^- + \text{O}_2$
12	2.0×10^7	3.0	$\text{OH}^- + \text{H} = e_{aq}^- + \text{H}_2\text{O}$
13	4.5×10^8	3.0	$e_{aq}^- + \text{H} + \text{H}_2\text{O} = \text{OH}^- + \text{H}_2$
14	6.3×10^7	3.0	$e_{aq}^- + \text{HO}_2^- + \text{H}_2\text{O} = \text{OH} + 2\text{OH}$
15	1.44×10^{11}	3.0	$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$
16	2.6×10^{-5}	3.0	$\text{H}_2\text{O} = \text{H}^+ + \text{OH}$
17	2.0×10^{10}	3.0	$\text{H} + \text{OH} = \text{H}_2\text{O}$
18	3.4×10^7	4.6	$\text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}$
19	2.70×10^7	3.4	$\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2$
20	4.4×10^7	4.5	$\text{H} + \text{H}_2\text{O}_2 = \text{OH} + \text{H}_2\text{O}$

Table 5. Cont.

No.	Rate Constant (L/Mol-s)	Activation Energy (Kcal/Mol)	Chemical Reactions
21	1.9×10^{10}	3.0	$H + O_2 = HO_2$
22	8.0×10^5	3.0	$HO_2 = O_2^- + H^+$
23	5.0×10^{10}	3.0	$O_2^- + H^+ = HO_2$
24	2.7×10^6	4.5	$2HO_2 = H_2O_2 + O_2$
25	1.7×10^7	4.5	$2O_2^- + 2H_2O = H_2O_2 + O_2 + 2OH$
26	2.0×10^{10}	3.0	$H + HO_2 = H_2O_2$
27	2.0×10^{10}	3.0	$H + O_2^- = HO_2$
28	1.8×10^8	4.5	$e_{aq}^- + O_2^- + H_2O = HO_2^- + OH$
29	1.8×10^8	4.5	$OH^- + H_2O_2 = HO_2^- + H_2O$
30	1.9973×10^{-6}	14.8	$2H_2O_2 = 2H_2O + O_2$
31	1.04×10^{-4}	3.0	$H + H_2O = H_2 + OH$
32	1.02×10^4	3.0	$H_2O + HO_2^- = H_2O_2 + OH$
33	1.5×10^7	4.5	$HO_2 + O_2^- = O_2 + HO_2$
34	7.7×10^{-4}	7.3	$H_2O_2 = 2OH$

Table 6. Nonviable reactions identified in various radiolysis mechanisms.

No.	Reaction	Elementary	Mass Balance	Charge Balance	Charge Viable
1	$e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^-$	No	Yes	Yes	No
2	$e_{aq}^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$	Yes	Yes	Yes	No
3	$e_{aq}^- + HO_2^- \rightarrow O^- + OH^-$	Yes	Yes	Yes	No
4	$e_{aq}^- + O^- + H_2O \rightarrow OH^- + OH^-$	Yes	Yes	Yes	No
5	$e_{aq}^- + O_3^- + H_2O \rightarrow O_2 + 2OH^-$	Yes	Yes	Yes	No
6	$O_2^- + O_2^- \rightarrow HO_2^- + O_2 + H^+$	Yes	No	No	No
7	$e_{aq}^- + HO_2^- + H_2O \rightarrow OH + 2OH^-$	Yes	Yes	Yes	No
8	$O_2^- + e_{aq}^- + H_2O_2 \rightarrow HO_2^- + OH^-$	No	No	Yes	No
9	$e_{aq}^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$	No	Yes	Yes	No
10	$e_{aq}^- + H_2O + NO_3^- \rightarrow NO_2 + 2OH^-$	No	Yes	Yes	No
11	$e_{aq}^- + H^+ + NO_2^- \rightarrow NO + OH^-$	No	Yes	Yes	No
12	$CuOH^{2+} + Cu^+ \rightarrow 2Cu^{2+} + OH^-$		Yes	Yes	No
13	$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+}$	Yes	Yes	Yes	No

The problematic reactions listed in Table 6 that are not elementary are deconvolved into two or more elementary reactions, as presented in Table 7. In all cases, the elementary reactions are already included in the models so that the problematic reactions are superfluous. They are most easily removed from the models by setting their rate constants equal to zero. Reaction (8), which does not mass balance, was taken from a widely employed model and does not appear to be a misprint because no changes in the stoichiometric coefficients can correct for the lack of mass balance. The reaction probably should have been written as $O_2^- + e^- + H_2O_2 \rightarrow O_2 + 2OH^-$, in which case it can be deconvolved as indicated in Table 7.

In reviewing the various models below, space does not allow us to list all the models individually. Instead, we include only those models where there is a specific, unequivocal reason for doing so. In the case of those models that are not listed, the reader is referred to the original source. We begin by identifying the non-elementary reactions that appear in almost all models that have been reported to date.

Most, if not all, radiolysis models postulate reactions between species having like charges [e.g., Reactions (8), (24), and (27), Table 4]. As noted previously, such reactions are generally unknown in chemistry under near-ambient conditions, except for outer-sphere charge (electron) transfer reactions [279], and should be excluded upon the basis of coulombic repulsion. Indeed, the whole objective of fusion is to achieve such reactions (e.g., $D^+ + T^+ \rightarrow He^{2+} + n$), but temperatures of the order of 300,000,000 K are required to do so!

Table 7. Deconvolution of nonviable reactions listed in Table 6 into elementary reactions.

No.	Reaction	Deconvolved Reaction
1	$e_{aq}^- + e^- + 2H_2O \rightarrow H_2 + 2OH^-$	$2(e_{aq}^- + H_2O \rightarrow H + OH^-)$ $H + H \rightarrow H_2$
2	$e_{aq}^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$	$e_{aq}^- + H_2O \rightarrow H + OH^-$ $H + O_2^- \rightarrow HO_2^-$
3	$e_{aq}^- + HO_2^- \rightarrow O^- + OH^-$	$HO_2^- \rightarrow OH + O^-$ $e_{aq}^- + OH \rightarrow OH^-$
4	$e_{aq}^- + O^- + H_2O \rightarrow OH^- + OH^-$	$e_{aq}^- + H_2O \rightarrow H + OH^-$ $H + O^- \rightarrow OH^-$
5	$e_{aq}^- + O_3^- + H_2O \rightarrow O_2 + OH^- + OH^-$	$e_{aq}^- + H_2O \rightarrow H + OH^-$ $H + O_3^- \rightarrow OH^- + O_2$
6	$O_2^- + O_2^- \rightarrow HO_2^- + O_2 + H^+$	$O_2^- + H_2O \rightarrow HO_2^- + OH^-$ $O_2^- + OH \rightarrow O_2 + OH^-$
7	$e_{aq}^- + HO_2^- + H_2O \rightarrow OH + 2OH^-$	$e_{aq}^- + H_2O \rightarrow H + OH^-$ $H + HO_2^- \rightarrow OH + OH^-$
8	$O_2^- + e_{aq}^- + H_2O_2 \rightarrow HO_2^- + OH^-$	$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$ $OH + O_2^- \rightarrow OH^- + O_2$
9	$e_{aq}^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$	$e_{aq}^- + H_2O \rightarrow H + OH^-$ $H + O_2^- \rightarrow HO_2^-$
10	$e_{aq}^- + H_2O + NO_3^- \rightarrow NO_2 + 2OH^-$	$e_{aq}^- + H_2O \rightarrow H + OH^-$ $H + NO_3^- \rightarrow NO_2 + OH^-$
11	$e_{aq}^- + H^+ + NO_2^- \rightarrow NO + OH^-$	$e_{aq}^- + H^+ \rightarrow H$ $H + NO_2^- \rightarrow NO + OH^-$

Any proposed model must ultimately account for the steady-state concentrations of the radiolysis products, as described by the stoichiometric equation for the reaction, as noted above. As also noted above, however, summation of the left sides and right sides of the reactions listed in Table 6, after including the source term, does not yield the stoichiometric equation for the decomposition of water. As a result, it is evident that neither charge balance nor mass balance is frequently attained. Obvious relationships must exist between the yields to maintain molar and charge balance simultaneously. The proposed models do not satisfy this fundamental requirement. The authors regard this to be a particularly important future modification of water radiolysis modeling.

While estimates of the standard reduction potentials (Table 8) and the standard Gibbs energies of formation of various inorganic radicals have been published [274], no electrochemical kinetic data are available except for the stable molecular radiolysis products, O_2 , and H_2 , and for unstable H_2O_2 . Kinetic theory is not sufficiently well developed at the present time to allow these data to be accurately calculated ab initio, but the problem is somewhat mitigated by the fact that the reactions involving minor (but highly reactive) species (e.g., H , OH) are under mass-transport control in determining the ECP. Accordingly, their participation in determining the ECP is readily incorporated by redefining the concentrations of H_2 , O_2 , and H_2O_2 , as noted above.

Table 8. Selected standard redox potentials for selected radicals [274].

Redox Couple	E^0/V_{she}	Redox Couple	E^0/V_{she}	Redox Couple	E^0/V_{she}
e_{aq}^-	−2.87	OH/H_2O	2.72	H_2O_2/H_2O	1.77
H/H^+	−2.31	H_2/H^+	0	O^-/H_2O	1.77
H/H^-	0.05	O_2/H_2O_2	1.23	O_2/O_2^-	−0.16
$(O_2, H^+)/HO_2$	0.12	O_3/O_3^-	0.83	O_2^+/O_2	3.2
NH_3^+/NH_3	2.13	NH_2/NH_2^-	0.7	NH_2OH^+/NH_2OH	≤1.26
NO^+/NO	1.21	NO_2/NO_2^-	1.04	NO_2^+/NO_2	1.51
NO_3^-/NO_3^{2-}	<−0.40	NO_3/NO_3^-	2.5	$N_2H_4^+/N_2H_4$	0.01
N_3/N_3^-	1.33				

The most extensive work on modeling the coolant chemistry of fission reactors, at least in terms of the numbers of operating reactors modeled, appears to be that reported by Macdonald et al. in the USA [216–234], Ibe and Ishigure in Japan [74,206,208,271], and by Yeh and co-workers in Taiwan [281–289], with the former dealing with fourteen operating BWRs and PWRs worldwide and the latter having modeled several BWRs, including Advanced BWRs, and a proposed Super Critical Water Reactor (SCWR) [288]. These models are now undergoing major refurbishment by inclusion of advanced submodels for calculating the ECP and damage due to stress corrosion cracking. A crack initiation model is also being developed [292].

Emphasis was initially placed on BWRs because of the rash of cracking incidents that have occurred historically in those systems. The radiolysis model (Table 5) and the set of G-values (Table 9) employed in [216–234,281–289] are essentially those found in [44], with the latter being updated from the work of Elliot [60]. In applying these models and data to modeling operating BWRs, the decomposition of hydrogen peroxide [Table 5, Reaction (30)] was employed as the calibrating reaction.

Table 9. G-values for primary radiolytic species at two temperatures used in the modeling of primary coolant in BWRs [215–252,255] (after Burns and Moore [44]).

No.	Species	25 °C		285 °C	
		G(n)	G(γ)	G(n)	G(γ)
1	e _{aq} [−]	0.93	2.70	1.08	4.15
2	H	0.50	0.61	0.66	1.08
3	H ⁺	0.93	2.70	1.08	4.15
4	OH	1.09	2.86	0.26	3.97
5	OH [−]	0.00	0.00	0.00	0.00
6	H ₂ O ₂	0.99	0.61	0.74	1.25
7	HO ₂	0.04	0.03	0.00	0.00
8	HO ₂ [−]	0.00	0.00	0.00	0.00
9	O ₂	0.00	0.00	0.00	0.00
10	O ₂ [−]	0.00	0.00	0.00	0.00
11	H ₂	0.88	0.43	0.00	0.62

Thus, the rate constant for Reaction 30, Table 5 was adjusted within the range of reported experimental values to account for the oxygen and hydrogen concentrations in the recirculation system of the Duane Arnold reactor. Once set, the model was found to accurately account for the recirculation system O₂ and H₂ for the full range of BWRs in the US fleet as well as for BWRs in Taiwan, Switzerland, Germany, and Spain. These reactors differ significantly in their response to hydrogen water chemistry (HWC), in which hydrogen is added to the reactor feedwater to “suppress radiolysis”, mimicking the long-standing practice in PWRs. Although HWC is not entirely successful, due to the volatility of hydrogen, which is stripped from the water by boiling in the core, the model did successfully predict the recirculation system oxygen concentration as a function of the hydrogen concentration in the reactor feedwater.

Strictly speaking, all G-values (*n*, *γ* and *α* radiation) for water must satisfy at any given moment, and under any physical conditions (temperature, solution composition), the conditions of mass balance for hydrogen:

$$-2G_{\text{H}_2\text{O}} = G_{\text{H}} + G_{\text{H}^+} + G_{\text{OH}} + G_{\text{OH}^-} + G_{\text{HO}_2} + G_{\text{HO}_2^-} + 2G_{\text{H}_2} + 2G_{\text{H}_2\text{O}_2} \quad (5)$$

mass balance for oxygen:

$$-G_{\text{H}_2\text{O}} = G_{\text{OH}} + G_{\text{OH}^-} + 2G_{\text{O}_2} + 2G_{\text{O}_2^-} + 2G_{\text{H}_2\text{O}_2} + 2G_{\text{HO}_2^-} + 2G_{\text{HO}_2} \quad (6)$$

and the condition of electroneutrality:

$$G_{e_{aq}^-} + G_{OH^-} + G_{HO_2^-} + G_{O_2^-} = G_{H^+} \quad (7)$$

Eliminating G_{H_2O} from Equations (5)–(7) yields:

$$G_{OH} + 2G_{OH^-} + 4G_{O_2} + 5G_{O_2^-} + 2G_{H_2O_2} + 4G_{HO_2^-} + 3G_{HO_2} = G_{e_{aq}^-} + G_H + 2G_{H_2} \quad (8)$$

It is practically impossible to obtain analytical relations (by using interpolation and extrapolation of experimental data for G-values that allow for satisfying Condition (8) strictly at any temperature (that can be important by performing multistep numerical calculations). To avoid this difficulty, the following procedure to redefining the G-values at any temperature was suggested [35]. Let us denote by SL a value on the left side of Equation (8) and by SR the corresponding value of right side. Accordingly, the value of $Sm = (SL + SR)/2$ is the average value of the left and right sides of Equation (8). Equation (8) holds if each G-value on the left side of Equation (8) is multiplied by the factor Sm/SL and each G-value on the right side is multiplied by the factor Sm/SR . After that, the value of G_{H^+} can be found via Equation (7). Calculations show that the differences between improved (obtained using this procedure) and initial G-values are usually within 1–1.5%.

The concentrations of the major radiolysis products (H_2 , O_2 , and H_2O_2) were used to estimate the ECP and CGR for IGSCC in sensitized Type 304 SS and, to the authors' knowledge, Macdonald et al. [216,218] were the first to have calculated the ECP and CGR using the MPM [217] and the CEFM [225], respectively. The CGR was then used to estimate the accumulated corrosion damage (crack length vs. time) as the reactor moves along the corrosion evolutionary path (CEP) [216,225–234,242–244], as discussed in detail in Part II [291]. These same calculations should be made for ITER because they provide a rational basis for specifying the optimal water chemistry protocol for minimizing corrosion damage and activity transport.

The radiolysis models briefly reviewed above are typical of all models that have been used to model the chemistry of the primary coolant of operating BWRs. These models have dealt with only radiolysis products comprising oxygen and hydrogen. However, one major problem in the application of HWC to BWRs is the generation of radioactive nitrogen isotopes ($^{16}N_7$ and $^{17}N_7$) via fast neutron irradiation of the naturally occurring isotopes of oxygen to affect the reactions $^{16}O_8(^1n_0, ^1p_1)^{16}N_7$ and $^{17}O_8(^1n_0, ^1p_1)^{17}N_7$ with the $^{16}N_7$ decaying back to $^{16}O_8$ via $^{16}N_7 \rightarrow ^{16}O_8 + \gamma + ^0e_{-1}$, resulting in the generation of energetic γ photons. The isotope $^{17}N_7$ decays as $^{17}N_7 \rightarrow ^{17}O_8 + ^0e_{-1} + ^1n_0$. These decays, under HWC conditions, can lead to high man-REM costs of reactor operation from the γ -radiation fields established in the turbine hall. Because the neutron capture cross section for $^{14}N_7$ is small (5.67 mb), resulting in the reaction $^{14}N_7(^1n_1, ^2n_1)^{13}N_7$ followed by decay of the daughter $^{13}N_7$ ($^{13}N_7 \rightarrow ^{13}C_6 + ^0e_{-1} + \gamma$), the possibility of the activation of the small amount of dinitrogen from the air in the coolant may be discounted. The reader is referred to Ref. [271] for a comprehensive discussion of this topic.

Examples of the prediction of the concentrations of O_2 , H_2O_2 , and H_2 in a BWR operating on NWC (left frames) and operating on moderate HWC are given in Figures 13–15, below. Two calibrations of the radiolysis code, RADIOCHEM [216,218,220], are displayed. One (solid line) is for the calibration on $[O_2]$ in an autoclave valved into the recirculation system while the other was for an abnormally high $[O_2]$ measured from the bottom drain of the RPV (broken line). Later analysis suggests that the first is the more reliable of the two. That study shows that the addition of H_2 at a feedwater concentration of 0.5 ppm significantly suppresses $[O_2]$ in the recirculation system (RS), core bypass (CB), and in the lower plenum (LP) but has only a minor impact on the rest of the circuit, particularly in the high radiation zones, such as in the core channels (CC) adjacent to the fuel bundles and above the core into which the radiolysis products are injected after being generated in the CC.

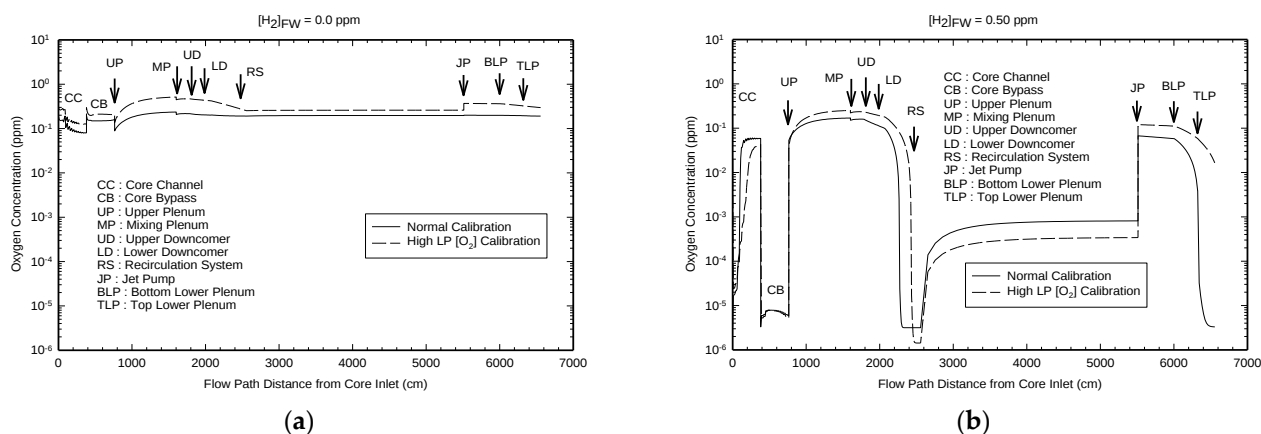


Figure 13. Calculated $[O_2]$ around a BWR PHTS for (a) NWC and (b) HWC with $[H_2]_{FW} = 0.5$ ppm. Note that two calibrations are included: the normal calibration on $[O_2]$ in the autoclave valved into the recirculation system and calibration of the $[O_2]$ measured in the LP.

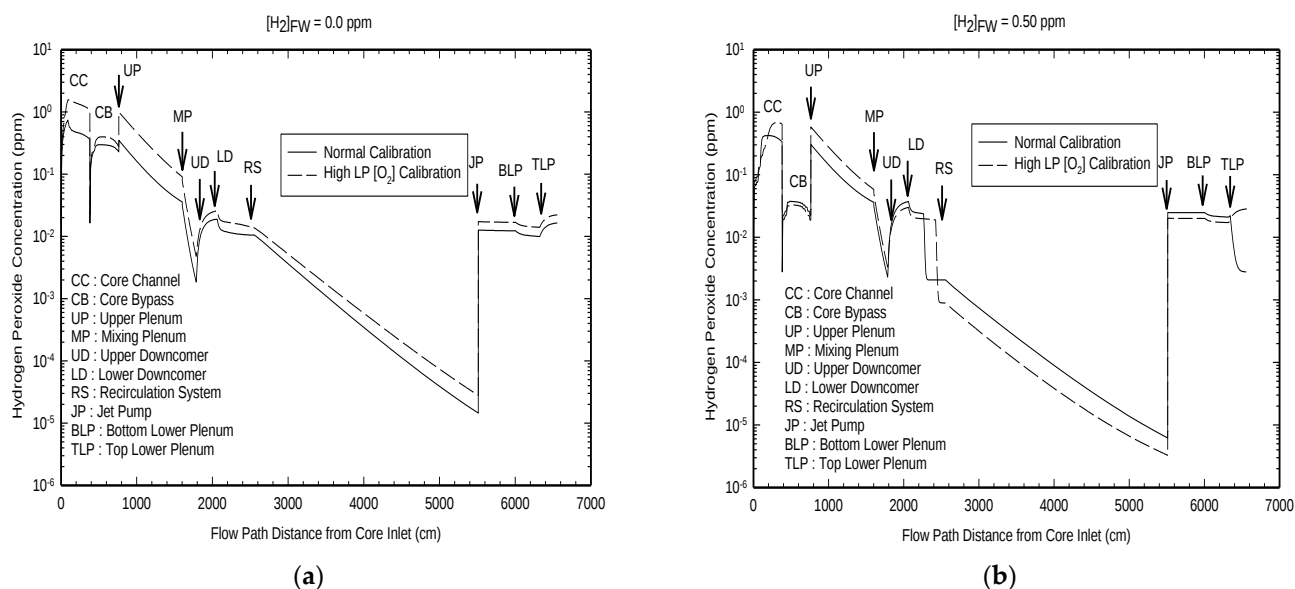


Figure 14. Calculated $[H_2O_2]$ around a BWR PHTS for (a) NWC and (b) HWC with $[H_2]_{FW} = 0.5$ ppm. Note that two calibrations are included: the normal calibration on $[O_2]$ in the autoclave valved into the recirculation system and calibration of the $[O_2]$ measured in the LP.

The fate of hydrogen peroxide is depicted in Figure 14. It is seen that the addition of H_2 to the feedwater at a concentration of 0.5 ppm has little impact on $[H_2O_2]$, a finding that has been noted elsewhere. Because hydrogen peroxide is the “bad actor” in BWR coolant circuits (because it is a much stronger oxidizing agent ($E^0_{HPER} = 1.77 V_{she}$) than is $[O_2]$ ($E^0_{OER} = 1.23 V_{she}$ at 25 °C)), this is an important finding as it is instrumental in determining the efficacy of HWC. However, recall that the contribution that any given redox species makes to the ECP and CGR is proportional to its concentration. The fact that the oxygen concentration is several orders of magnitude greater than that of hydrogen peroxide somewhat mutes the greater oxidizing power of the latter. Another factor that contributes to the high $[O_2]$ and $[H_2O_2]$ above the core and in the CCs is the fact that H_2 , having a much lower molecular weight (MW = 2.016 g/mol) than O_2 (MW = 32 g/mol) and H_2O_2 (MW = 34.016 g/mol) is more readily stripped by boiling into the steam phase and hence is not present in the liquid water coolant in these regions to affect the suppression of the radiolysis of liquid water.

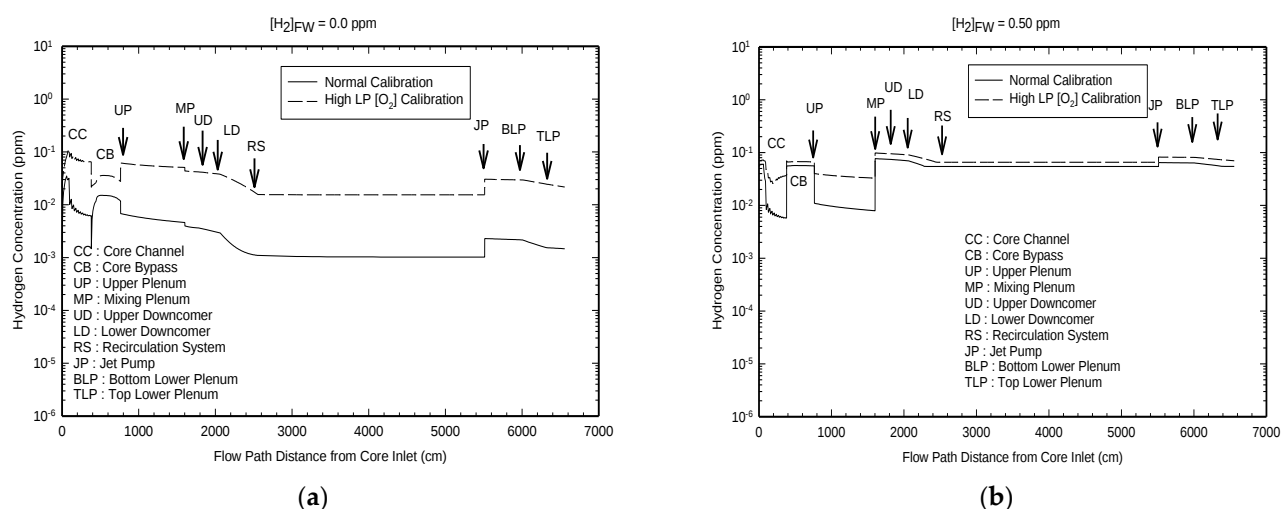


Figure 15. Calculated $[H_2]$ around a BWR PHTS for (a) NWC and (b) HWC with $[H_2]_{FW} = 0.5$ ppm. Note that two calibrations are included: the normal calibration on $[O_2]$ in the autoclave valved into the recirculation system and calibration of the $[O_2]$ measured in the LP [233].

The predicted hydrogen concentration around the coolant circuit is displayed in Figure 15. Concentrating on the normal calibration, we note that the $[H_2]$ under NWC (no hydrogen added to the feedwater) ranges from about 30 ppb in the CCs and slightly lower in the core bypass (CB) down to 1 ppb in the recirculation system. This hydrogen is produced entirely by the radiolysis of water because no hydrogen is added to the feed water.

The low $[H_2]$ in the RS reflects the fact that coolant from which the H_2 has been stripped in the core by boiling flows down the downcomer and then into the RS. In the case of the reactor on HWC, $[H_2]$ is 1–2 orders of magnitude higher and is controlled by the hydrogen added to the feedwater. Nevertheless, $[H_2]$ is still predicted to vary around the circuit by about an order of magnitude, and this variation can be understood in terms of the stripping of hydrogen from the coolant by boiling in the core. The features described above have, in general, been predicted and observed for all fourteen BWRs that have been modeled in our group over the past three decades, with only relatively minor differences between different reactors. In Part II of this review [291], data of the type shown in Figures 13–15 are used to predict the ECP and CGR for IGSCC in sensitized Type 304 SS in operating plants. It is shown that HWC can have a significant impact on the mitigation and the accumulation of IGSCC damage in certain locations (e.g., RS, LP) but not in others (e.g., UD) and that the reasons for the differences are well understood in terms of the electrochemistry of the system.

4. Previous Radiolysis Models for ITER

Several models have been developed for describing the chemistry/radiolysis of water in the ITER PHTS [1,25–28,31], some of which are discussed below. These models are generally extensions or adaptations of the models that have been employed for modeling the primary coolant circuits of water-cooled fission reactors, including BWRs, PWRs, VVERs, and CANDUs, so listings of the reactions in each model are not given here because of the limitations in space. Instead, the reader is referred to the original publications for mechanistic details. However, close examination of these models shows that they suffer from the same maladies as do the fission reactor radiolysis models, as discussed above. This is illustrated below regarding two specific models.

Before reviewing the previous work on modeling the radiolysis of water in the ITER, it is first necessary to briefly discuss some important differences in the radiation produced by nuclear fissioning of $^{235}U_{92}$ by thermal neutrons, as in water-cooled and moderated fission reactors, and the fissioning of the isotopes of hydrogen. The fissioning of $^{235}U_{92}$ may be described by the reaction $^{235}U_{92} + {}^1_0n \rightarrow {}^{144}Ba_{56} + {}^{89}Kr_{36} + 3{}^1_0n$, which is sometimes

written as $^{235}\text{U}_{92} + ^1\text{n}_0 \rightarrow ^{134}\text{Xe}_{54} + ^{100}\text{Sr}_{38} + 2^1\text{n}_0$, where the energy of the prompt neutrons is 4.8 MeV. A spectrum of γ -photon of 15–25 MeV is also emitted, and the total energy release including delayed emission is 211.3 MeV, corresponding to a 0.093% conversion of mass into energy [% mass conversion = $0.4255(E/c^2)$, Table 1]. Thus, the radiation in light or heavy water-moderated fission reactors, such as a BWRs, PWRs, VVERs, and CANDUs, comprises neutrons and γ -photons. In the case of a PWR, which employs a boric acid nuclear “shim” to control core reactivity via the neutron absorbing reaction $^{10}\text{B}_5(^1\text{n}_0, ^4\text{He}_2)^7\text{Li}_3$, the resulting α particles ($^4\text{He}_2$) contribute significantly to the total energy dose rate. In the case of nuclear fusion, the D–T reaction has the lowest ignition temperature and may be written as $^2\text{H}_1 + ^3\text{H}_1 \rightarrow ^4\text{He}_2$ (3.5 MeV) + $^1\text{n}_0$ (14.1 MeV) to yield a total energy of 17.6 MeV, with a mass-to-energy conversion of 0.386% (Tables 1 and 2). A fusion reactor will also produce a considerable γ -photon dose rate from the plasma, as further noted below. The penetrating power of the different forms of radiation in water are measured by the LET values summarized in Table 10, along with typical dose rates for the various forms of radiation. The G-values given in [52] are summarized in Table 11 as a function of LET.

Table 10. Dose rate and LET of various forms of radiation in the radiation zone of the ITER [52,53].

Radiation Type	LET/eV·nm ^{−1}	Inlet Dose Rate 10 ²² eV/dm ³ ·s	Central Dose Rate 10 ²² eV/dm ³ ·s	Outlet Dose Rate 10 ²² eV/dm ³ ·s
Gamma	0.2	0.130	0.842	0.130
Proton	35	0.74	6.52	0.74
Neutron	100 (14.1 MeV)	—	—	—
Triton	24	1.96	14.8	1.96
Alpha	180	1.46	11.2	1.46

Table 11. Radiolytic yields as a function of LET (after Elliot, et al. [52,53]).

LET/eV nm ^{−1}	G						
	−H ₂ O	e [−] _{aq}	OH	H	H ₂	H ₂ O ₂	HO ₂
0.23	4.08	2.63	2.72	0.55	0.45	0.68	0.008
12.3	3.46	1.48	1.78	0.62	0.68	0.84	—
61	3.01	0.72	0.91	0.42	0.96	1.00	0.05
108	2.84	0.42	0.54	0.27	1.11	1.08	0.07

The values listed in Table 11 were taken from [52,53] and strictly apply to irradiation in the aqueous LiOH blanket for the breeding of tritium. In this system, the various forms of irradiation include γ -photons and recoil ions from the interaction of high-energy neutrons with steel, water, and triton (tritium, $^3\text{H}_1$) and alpha ($^4\text{He}_2$) particles from the neutron fission reaction with $^6\text{Li}_3$ ($^6\text{Li}_3 + ^1\text{n}_0 \rightarrow ^3\text{H}_1 + ^4\text{He}_2 + 4.78$ MeV). Note that the more massive particles have the largest LET, and hence on a unit energy basis, they are the least penetrating. However, LET is important because the primary radiolytic yields (G_i^p) depend on LET, and therein lies an important difference between fusion and fission reactors. Thus, fission reactors operate with much fewer energetic neutrons (4.8 MeV down to a few tenths of an eV for “thermalized” neutrons) than does a fusion reactor (14.1 MeV), so the primary radiolytic yields are expected to be significantly different for a fusion reactor than those for a fission reactor.

One major issue that arises from coolant radiolysis in ITER is the dissociation of water into gaseous hydrogen and oxygen [1,25,35,37,50,77,94,96]. This issue has been recently addressed by radiolysis modeling in [1,35]. Accumulation of these gases in a tank could potentially lead to accident scenarios. Furthermore, if oxygen is allowed to accumulate unimpeded, it represents a corrosion hazard, particularly toward copper alloys. Two approaches may be adopted to reduce or even eliminate this risk: (1) continuous vacuum

degassing, as was practiced in some BWRs, and (2) hydrogen additions to the coolant, as is practiced in PWRs and in BWRs operating on hydrogen water chemistry (HWC).

Although there are three PHTSs in ITER (see Figure 8), Sato et al. [25] chose to model the blanket cooling system (which is part of today's IBED PHTS) because it will experience the highest irradiation dose rates from the 14.1 MeV neutrons and the 15–25 MeV gamma photons produced by D–T fusion. A schematic of the blanket flow system is given in Figure 16. Only one of the three identical blanket cooling loops was modeled. As seen in Figure 16, the cooling water enters the upper side of the blanket, then circulates within the blanket, and exits to the HX from the upper side of the blanket again. The blanket comprises many tubes (called “blanket modules,” Figure 16), and although the flow rate is different through each module, an average value was used for the sake of simplicity.

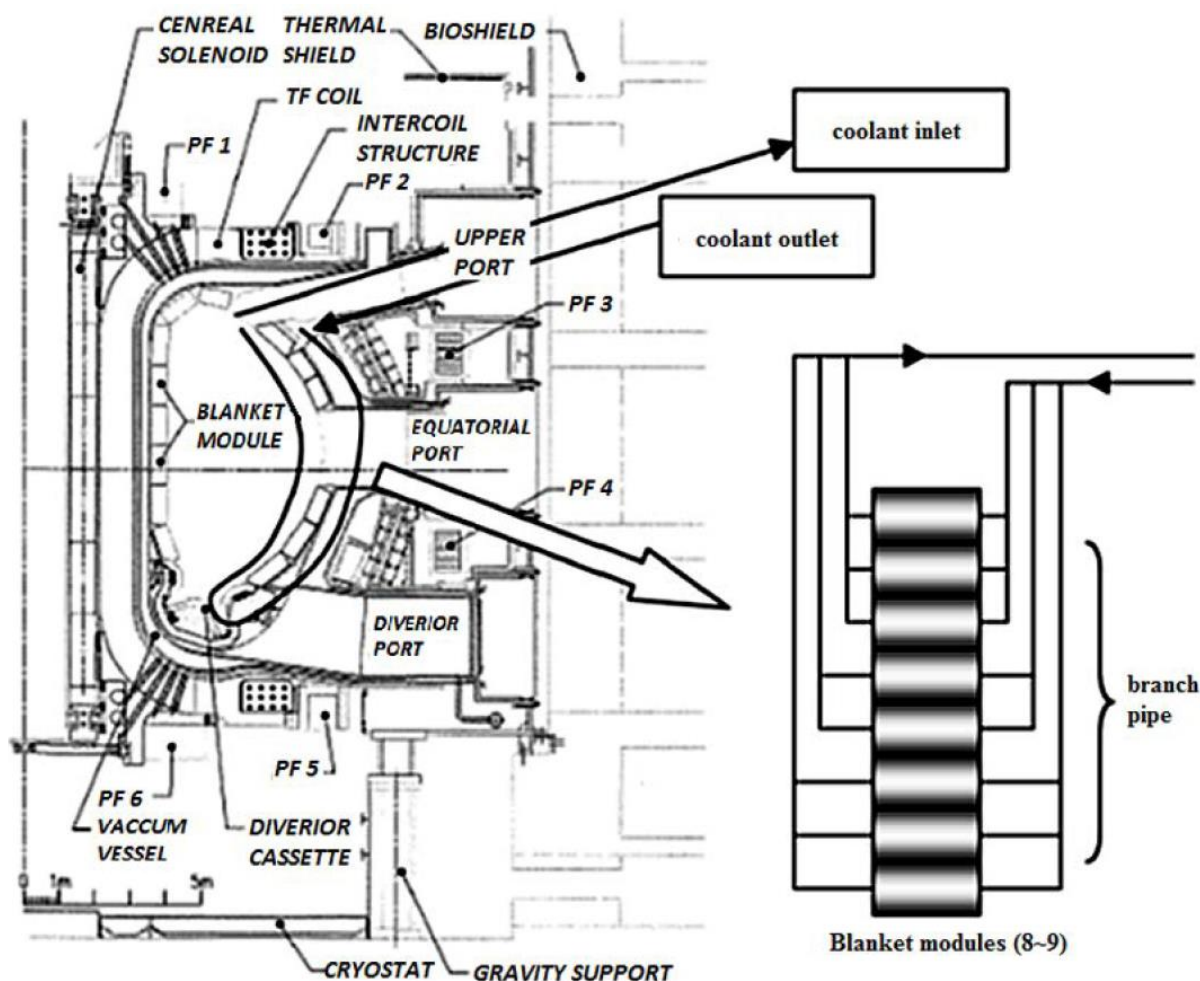


Figure 16. Cooling flow loop for the blanket cooling system (after Sato et al. [25]). ©2006 ITER Organization. This image is hereby used courtesy of the ITER Organization.

The sequence of materials to which the coolant is exposed as it flows through the blanket PHTS are stainless steel plate at the inlet, a copper heat sink, stainless steel plate, another stainless steel, a copper heat sink, and stainless steel corresponding to the outlet stainless steel plate, the Cu heat sink, and finally a stainless steel shield block at the coolant outlet. Thus, the materials represent a mixture of stainless steels and copper. If the conditions achieved within the coolant are highly reducing, via the addition of hydrogen to effectively “suppress” radiolysis and hence the production of oxygen and hydrogen peroxide, copper will be immune to corrosion if the electrochemical potential is displaced below the equilibrium potential for the Cu^+/Cu reaction for a given activity of Cu^+ , except

if the coolant contains an activating species, such as bisulfide ion (HS^-) or a complexing species such as ammonia (NH_3). Given that ammonia is generated by neutron capture by oxygen, this latter possibility is an important issue that needs to be addressed in any future work. Furthermore, dissolved copper is known to plate out on stainless steels via a displacement reaction and induce pitting attack on the steel. This illustrates the “law of unintended consequences” when choosing multiple materials for service in a coolant system.

Table 12 summarizes the parameters used in [25] to model the blanket PHTS in ITER. The coolant is pure water of $\text{pH} = 7$ at 25°C , to which is added 2 ppm of hydrogen. For comparison with a typical PWR PHTS, this concentration amounts to $22.4\text{ cm}^3(\text{STP})/\text{kg H}_2\text{O}$, which is at the lower end for current PWR operation ($20\text{--}35\text{ cm}^3(\text{STP})/\text{kg H}_2\text{O}$), but is significantly greater than that of a BWR operating under the HWC protocol (typically $0.5\text{--}1.0\text{ ppm H}_2$). However, no pH control, as exists in PWR primary coolant, is currently proposed for ITER. Therefore, the proposed water chemistry is best described as corresponding to Super Hydrogen Water Chemistry (SHWC) without boiling, which is ensured by the pressure of 3 MPa (30 atm). A flow rate of $1.74 \times 10^3\text{ kg/s}$ is assumed for the modeled loop. From the volumes of each section and the flow rates, transit times for the water in various regions of the circuit are calculated to be 1.29 s, 5 s, and 71.62 s. Most time is spent in the nonradiated regions. The absorbed neutron irradiation energy is taken to be $2.1 \times 10^{-2}\text{ W/g}$ and $1.5 \times 10^{-3}\text{ W/g}$ in the two principal radiation zones, while the corresponding values for gamma photons are 2.7×10^{-3} and $4.8 \times 10^{-4}\text{ W/g}$, which are typical of BWRs, but are lower than for a PWR. Thus, from a core specific power viewpoint, ITER is like a BWR. However, the energy spectra for neutrons and gamma photons are quite different between fission and fusion reactors, as has been noted above.

Table 12. Analytical conditions assumed in [25] in modeling the production of H_2 and O_2 in the blanket PHTS of ITER.

Condition	Contents	Note
Liquefaction of water	Pure water ($\text{pH} = 7$)	
Temperature	Dissolved hydrogen 2 ppm Nonradiated field: 100°C Irradiated field: 150°C	
Pressure	3 MPa	
Flow rate	1.74 ton/s	/1 panel of FW
Passage time	(1) $1.29\text{ s} \times 2$ (2) $5\text{ s} \times 2$ (3) 71.62 s	Set up from tube layout and flow rate
Circulation time	84.2 s	
Absorption energy	(1) Neutron: $2.1\text{ E-}2\text{ W/g}$ γ : $2.7\text{ E-}3\text{ W/g}$ (2) Neutron: $1.5\text{ E-}3\text{ W/g}$ γ : $4.8\text{ E-}4\text{ W/g}$	

Three sets of irradiation conditions were modeled by Sato et al. [25], with the irradiation fields being identified in Figure 17. Table 11 summarizes the energy dose rates of neutrons and gamma photons in the two radiation fields as a function of time for any element of the coolant.

The modeled radiolysis of the coolant in the blanket PHTS of ITER as a function of the radiation zone at a temperature of 150°C and for (added) hydrogen concentration of 2 ppm ($1 \times 10^{-3}\text{ m}$) is presented in Figure 18 [25]. As expected, radiolysis occurs most intensively in Region 1, which is subjected to the highest energy dose rate (Figure 19). On passing into Region 2, where both the neutron and gamma dose rates are lower (Figure 18), the concentrations of the radiolysis products are lower, particularly the concentrations of

OH and O₂, but the decrease in the concentration of H₂O₂ is quite modest. On entering the nonradiated zone, the concentrations of all radiolysis products are sharply reduced, except that of hydrogen peroxide. Note that the rate of thermal decomposition of H₂O₂ at 150 °C is slow and accounts for the persistence of hydrogen peroxide into the nonradiated zone. These results are in line with similar work carried out on fission reactors, as discussed above.

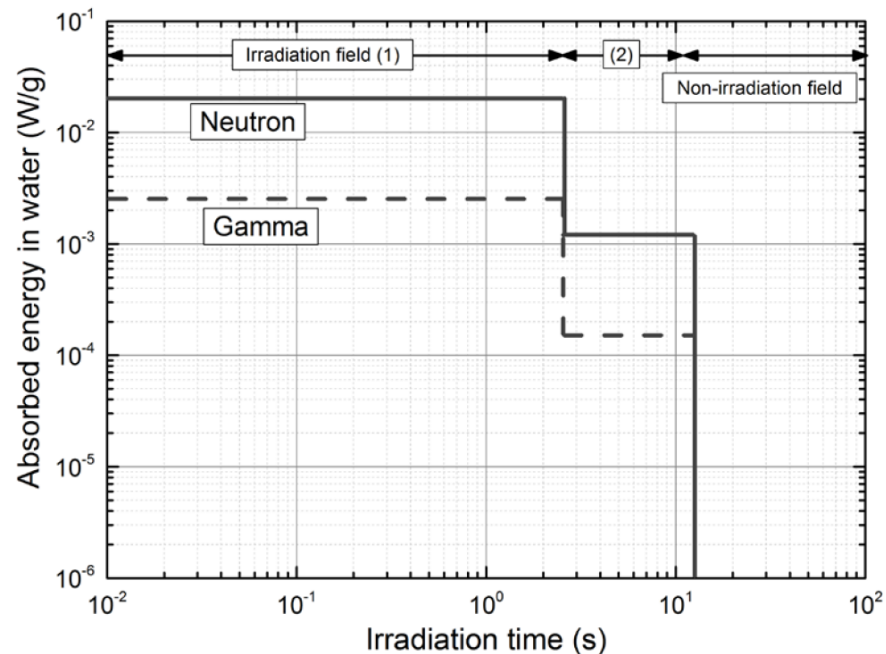


Figure 17. Energy dose rates of neutrons and gamma photons in the two radiation fields assumed in [25]. ©2006 ITER Organization. This image is hereby used courtesy of the ITER Organization.

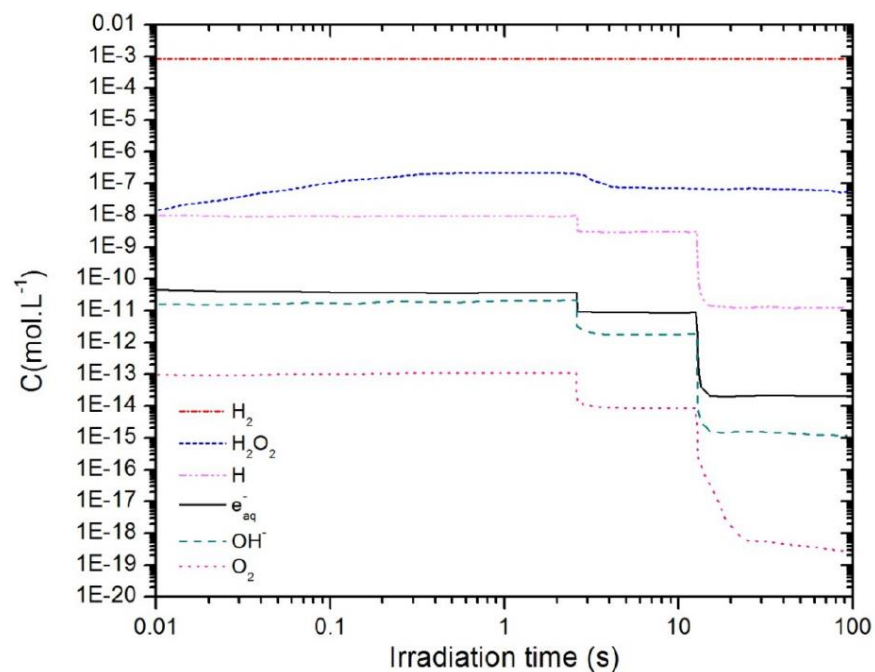


Figure 18. Predicted concentrations of radiolysis products with the passage of the coolant through the three radiation zones for Case 1. [H₂] = 2 ppm, T(irradiation zone) = 150 °C, T(nonradiated zone) = 100 °C, absorbed energy: Field 1; 0.021 W/g (n); Field 2; 0.0015 W/g (γ) (after Sato et al. [25]). ©2006 ITER Organization. This image is hereby used courtesy of the ITER Organization.

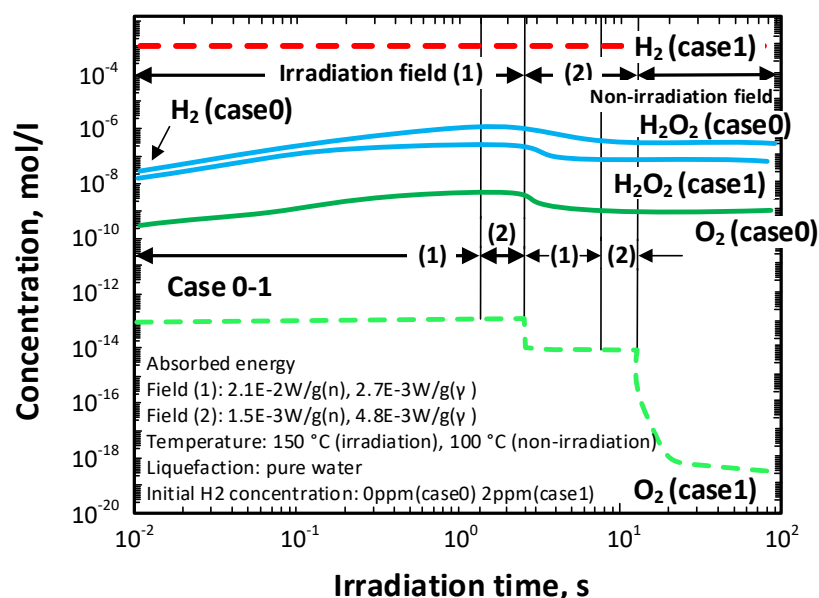


Figure 19. Predicted concentrations of radiolytic species in the ITER blanket PHTS cooling water without (Case 0) and with (Case 1) the addition of 2 ppm (1×10^{-3} m) hydrogen (after Sato et al. [25]). ©2006 ITER Organization. This image is hereby used courtesy of the ITER Organization.

Figure 19 shows a comparison between the radiolysis behavior of the coolant without hydrogen (Case 0) and with 2 ppm of hydrogen (Case 1). Hydrogen effectively suppresses the formation of oxygen but is predicted to be only modestly effective in suppressing the formation of hydrogen peroxide. Because H_2O_2 is a much stronger oxidizing agent than is O_2 , and because it contributes more on a molar basis to establishing a high ECP, weak suppression of H_2O_2 can have important consequences for corrosion. However, these consequences are not directly reflected in the concentrations of the radiolysis products but are reflected in the ECP, which is readily calculated from the concentrations using a mixed potential model [216–218]. Thus, it is known that all forms of general corrosion (GC) and localized corrosion (LC), including pitting corrosion (PC), crevice corrosion (CC), stress corrosion cracking (SCC), corrosion fatigue (CF), and hydrogen-induced cracking (HIC), all occur at potentials that are more positive than critical values (more negative in the case of HIC) that depend on the temperature, the thermo-mechanical history of the substrate, and the composition of the alloy. Thus, the strategy for avoiding future corrosion damage requires the use of a water chemistry protocol together with an appropriate alloy that places the ECP as being more negative than the critical potentials for PC, CC, SCC, and CF, but more positive than the critical potential for HIC. A discussion of this important topic is beyond the scope of this review, but the principles supporting this approach will be discussed in Part II [291].

In summary, the work presented in Sato [25] has raised several critical issues, including the need for more accurate radiolytic yield data (i.e., primary G-values), particularly for 14 MeV neutrons of high LET. However, it is evident that the study authors were not conversant with corrosion issues or how these are impacted by the radiolysis of water. They also appear to be unaware of the extensive work published on water radiolysis in water-cooled fission reactors and how that phenomenon impacts corrosion and plant operation, as reviewed above. In the authors' opinion, the radiolysis work published to date on fusion reactors is in the same stage of development as was that for fission reactor work in the mid-1990s. Thus, the authors found only one reliable attempt to calculate the ECP [253] and no attempts to calculate the rates of growth of stress corrosion cracks, something that was achieved in the mid-1990s in modeling fission reactors [215–252,255,281–289], although the SCC of stainless steels had been addressed experimentally [23].

Kritsky et al. [27] report a study of radiolysis in the Divertor PHTS (which is part of today's IBED PHTS) assuming the water chemistry parameters that existed at that time (summarized in Table 13). The coolant is essentially pure water that is similar to the feedwater of a BWR, except for the added hydrogen; in this case, the coolant may be classified as being SHWC in character, as noted elsewhere. It is apparent that these authors were aware of the importance of the ECP because they list it in the table, albeit without specifying a value.

Table 13. Water chemistry parameters for the Divertor PHTS coolant [27].

Parameters of Water Reactor during Operation	Feedwater	Values to Start Plasma Ignition	Upper Limits for Action
Conductivity (at 25 °C), uS/cm	<0.1	<0.1	<0.3
Hydrogen (cm ³ /kg at STP) (ppm)		~25 ~2	
Electrochemical Corrosion Potential (mV SHE)		TBD	<TBD
Oxygen (ppb)	<20	<1	<10
Chloride and Fluoride (ppb)	<0.5	<1	<5
Sulfate (ppb)	<20	<2	<5
Copper (ppb)	<0.5	<5	<5
Iron (ppb)	<1		<5
Hardness (Ca, Mo, etc.) (ppb)	<5		<5
Oil products, organic (ppb)	<100		<100

Four pre-existing radiolysis codes—FACSIMILE, MAKSIMA, CHENSIMUL, and ITERh—with their attendant reaction and parameter sets, were employed [27]. Although Kritsky et al. [27] state that the reactions are all elementary, this is not correct because certain reactions may be decomposed into actual elementary reactions, as noted above. Additionally, the reaction set contains reactions between species of like charge, which are unknown in the annals of chemistry under near-ambient conditions, except in the case of outer sphere charge (electron) transfer reactions [273] because of the strong coulombic repulsion. As shown in Figure 20, the G-values depend on the LET, with the LET increasing with the kinetic energy of the ionizing particle and hence with mass (and velocity). Thus, γ -photons and β particles (i.e., electrons) tend to be low LET forms of radiation while ionized atoms (e.g., α -particles and C^{6+}) generally possess high LET. As also shown in Figure 20, the G-values decrease with increasing LET, except for H_2 , H_2O_2 , and O_2^- , which all show weak increases. The species for which the G-values are found to decrease with increasing LET [H^+ , e_{aq}^- , OH , and H ($LET > 0.2$ eV/A)] all result from the initial interaction of ionizing radiation with water, whereas those whose G-values tend to increase with increasing LET (i.e., O_2 , H_2 , and H_2O_2) result from reactions at longer times (Table 4). This behavior clearly indicates that the yield reflects a competition between the rate of formation (due to fragmentation of water) and the rate of consumption (as evidenced by reaction within the spur) with consumption dominating at higher LET, resulting in a decrease in the yield. In the case of atomic hydrogen, however, at lower LET levels, the rates of these processes are equal, and the yield is essentially independent of LET (Figure 20). It is also likely that the data summarized in Figure 20 are strictly not primary yields, as defined above, because data for species other than those formed in the spurs (Table 4) are also listed.

The set of G-values employed by Kritsky et al. [27] for a temperature of 250 °C were taken from Elliot [51] and others [73,87,146]. The dose rates employed were $1 \text{ Gy/s} = 100 \text{ rad/s} = 6.25 \times 10^{18} \text{ eV/(L}\cdot\text{s)}$ or $10^4 \text{ Gy/s} = 10^6 \text{ rad/s} = 6.25 \times 10^{22} \text{ eV/(L}\cdot\text{s)}$, and the oxygen concentration in the feedwater was assumed to be 0 or 0.25 mM.

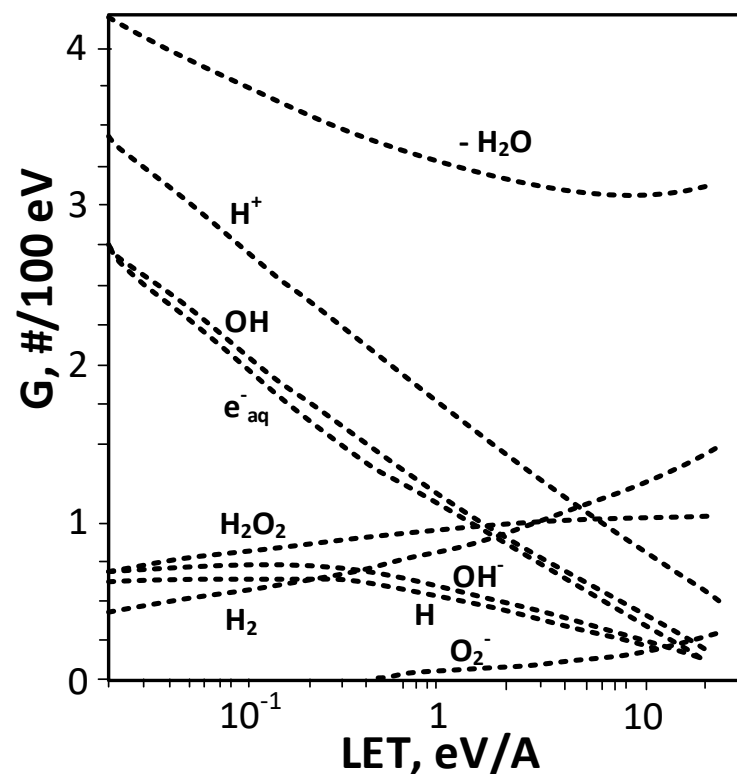


Figure 20. G-values for various radiolysis products as a function of LET (after Kritsky et al. [27]). ©2001 ITER Organization. This image is hereby used courtesy of the ITER Organization.

Table 14 presents results obtained using FACSIMILE for neutron and gamma irradiation for equivalent dose rates. These results demonstrate that high-energy neutrons are about 10–20 times more effective in producing H_2 , O_2 , and H_2O_2 than are gamma photons at an equivalent dose rate.

Table 14. Concentrations of H_2 , O_2 , and H_2O_2 predicted by [27] by gamma and neutron irradiation at equivalent dose rates of 10^4 Gy/s.

Type of Irradiation	Dose Rate (Gy/s)	$[H_2]$ (μM)	$[O_2]$ (μM)	$[H_2O_2]$ (μM)
Gamma	10^4	5.5	0.078	2.0
Neutron	10^4	50	0.800	40.0

A detailed view of the impact of dose rate of γ -irradiation (a) and fast neutron irradiation (b) on the yields of H_2 , O_2 , and H_2O_2 is afforded by the predictions of Kritsky et al. [27] is plotted in Figure 21. Again, the factor of 10–20 difference in the yields is apparent between gamma (a) and neutron (b) irradiation, but the most surprising prediction is the presence of maxima in the yield of O_2 and to a lesser extent in the yields of H_2 and H_2O_2 under neutron irradiation at a dose of 10^3 to 10^4 Gy. Additionally, the study authors postulate a species “ H_2O_3 ” (i.e., trioxidane) in the case of γ -irradiation (a), which they posit forms via the reaction $OH + HO_2 = H_2O_3$. While this species is known to exist, particularly in biological systems, the current review found no evidence for its existence in irradiated water. If the maxima in the yields is not a computational artifact, the result may indicate a preference for the recombination of O_2 and H_2O_2 with hydrogen at high dose rate over and above their generation, which dominates at low dose. A similar phenomenon is observed in BWRs, for example, but is normally couched in terms of dose, and results from a spatial distribution of radiolysis associated with different in-vessel regions. Thus, in BWRs, recombination of O_2 and H_2O_2 is postulated to occur in the downcomer on the outside of the core shroud. In that case, the destruction of H_2 , O_2 , and H_2O_2 is “catalyzed” by the lower level of radiation

in the downcomer, which is nevertheless sufficiently intense to catalyze the reactions via a free-radical mechanism.

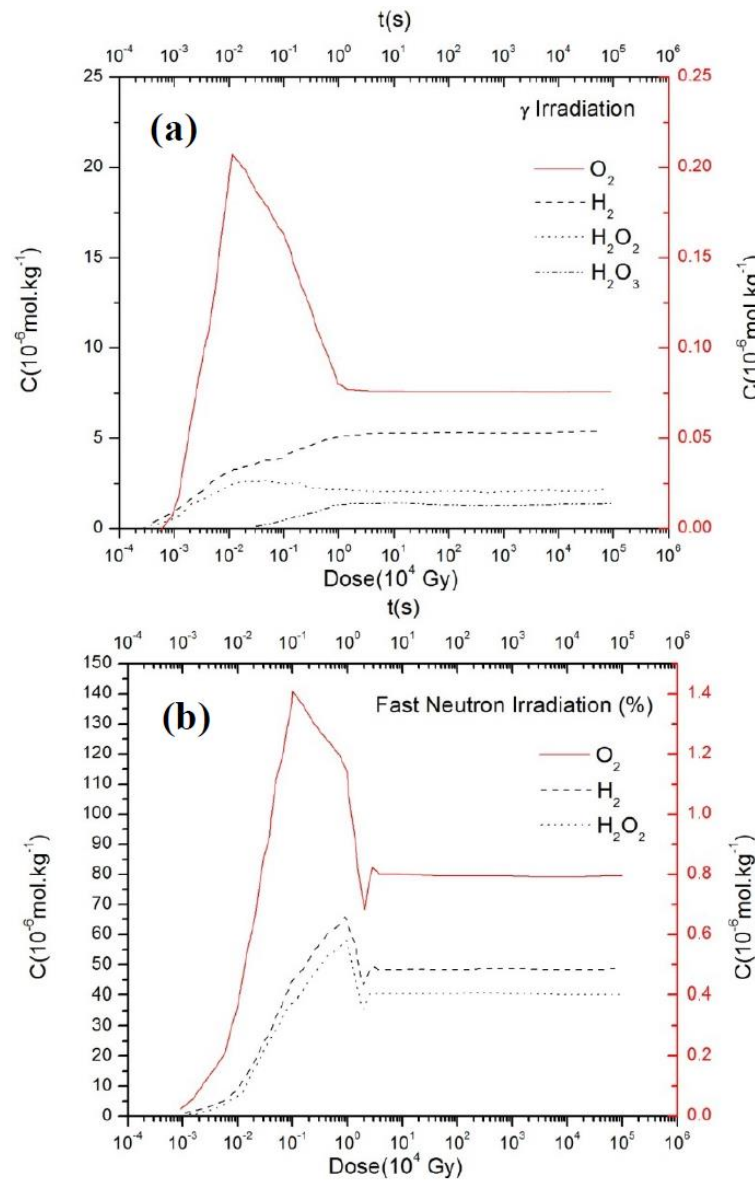


Figure 21. Calculated concentrations of H_2 , O_2 , H_2O_2 and “ H_2O_3 ” as a function of dose of γ -radiation (a) and fast neutrons (b) at a dose rate of 10 kGy/s at 250 °C (after Kritsky et al. [27]). ©2001 ITER Organization. This image is hereby used courtesy of the ITER Organization.

Table 15 presents the calculated results of Kritsky et al. [27] with respect to the impact of added hydrogen on the concentrations of H_2 , O_2 , and H_2O_2 for γ -radiation at a fixed dose rate of 1 Gy/s.

Table 15. Effect of added hydrogen on the predicted concentrations of H_2 , O_2 , and H_2O_2 . (after Kritsky et al. [27]).

Type of Irradiation	D(Gy/S)	$[\text{H}_2](\text{M/L})$	Steady-State Concentrations ($\mu\text{M/L}$)		
			H_2	O_2	H_2O_2
γ	1	0	2×10^{-5}	3×10^{-4}	10^{-4}
γ	1	10^{-3}	0.8×10^{-3}	10^{-16}	3×10^{-8}

While the hydrogen concentration naturally increases, because hydrogen is being added to the system, the concentration of oxygen is predicted to be suppressed by almost twelve orders of magnitude. The impact on the hydrogen peroxide concentration is predicted to be much less (about four orders in magnitude), but, nevertheless, the large impact on $[O_2]$ has justified the claim that the addition of hydrogen “suppresses radiolysis. This relationship between radiolysis and added hydrogen was well defined in previous work on modeling radiolysis in BWRs and PWRs [216 and references therein], but this conclusion must be accepted with a word of caution. This is because the benefits of added hydrogen are not so much through the suppression of the concentrations of O_2 and H_2O_2 per se, but its impact on the ECP. Thus, H_2O_2 is a much more powerful oxidizing agent than is O_2 ; that is, it possesses a much more positive standard reduction potential of $1.77 V_{she}$ vs. $1.23 V_{she}$, respectively, and hence has a much greater impact on the ECP than does the addition of oxygen for equivalent molar concentrations. Furthermore, experiments have shown that the addition of small amounts of oxidizing agents to hydrogenated water can result in a significant shift of the ECP in the positive direction [253]. Clearly, the most important species in affecting this shift is H_2O_2 , and the extent to which any species contributes to the shift in the ECP is roughly proportional to the concentration, as determined by the contribution of the partial current density the reduction or oxidation of that species to the total partial current flowing at the interface under open circuit conditions. As seen in Table 14, the concentration of oxygen under hydrogenation conditions is almost twelve orders of magnitude lower than that of H_2O_2 , so that oxygen has no impact on the ECP, but hydrogen peroxide does have a significant impact because its concentration is predicted to be lowered by less than four orders in magnitude. Finally, it is important to recognize that the ECP is a mixed potential established by the balance of charge transfer (i.e., redox) reactions involving oxidizing and reducing species at the metal surface, including the passive electro-dissolution of the metal itself. Theory shows [217] that the ECP will lie closest to the equilibrium potential of the redox couple that has the highest exchange current density. Because the exchange current density (i_0) shows a positive relationship with the concentrations of R and O for the redox reaction $R = O + ne^-$ of the type $i_0 = i_0^0 \left(C_O^b \right)^\alpha \left(C_R^b \right)^{1-\alpha}$ where i_0^0 is the standard exchange current density, which is independent of the composition of the solution, C_O^b and C_R^b are the concentrations of the redox species O and R in the bulk environment, respectively, and α is the transfer coefficient of the reaction (a constant). Thus, if one species (e.g., H_2) is present in great excess, regardless of whether radiolysis has been “suppressed,” the ECP will lie closest to the equilibrium potential for the HER. Thus, even though the “suppression of radiolysis” may occur, it is not a necessary condition for the displacement of the ECP in the negative condition; all that is required is that the concentration of hydrogen in the coolant be much greater than the concentrations of any oxidizing species. This condition is always fulfilled in PWR coolant chemistry conditions but is not fulfilled in BWRs operating on NWC (i.e., no added hydrogen) or even on hydrogen water chemistry (HWC, 0.5–1 ppm added to the feedwater). This important fact is seldom recognized in reactor technology.

ITER is a mixed irradiation system, where both fast (14.1 MeV) neutron and γ -photon irradiation impact the chemistry and electrochemistry of the coolant water. Kritsky et al. [27] explored this issue, and their results are presented in Figure 22, which compares the predicted radiolysis product concentrations for NWC (i.e., zero added hydrogen) and HWC (i.e., $[H_2] = 10^{-3} M$) as a function of irradiation mix. These calculations demonstrate the higher yields of radiolysis products under fast neutron irradiation compared with γ -photon irradiation, this being by the higher LET of the former than of the latter. However, the calculations suggest a synergistic effect of mixed irradiation on the ability of hydrogen to suppress radiolysis. The authors have not been able to locate any experimental data that confirm this interesting prediction.

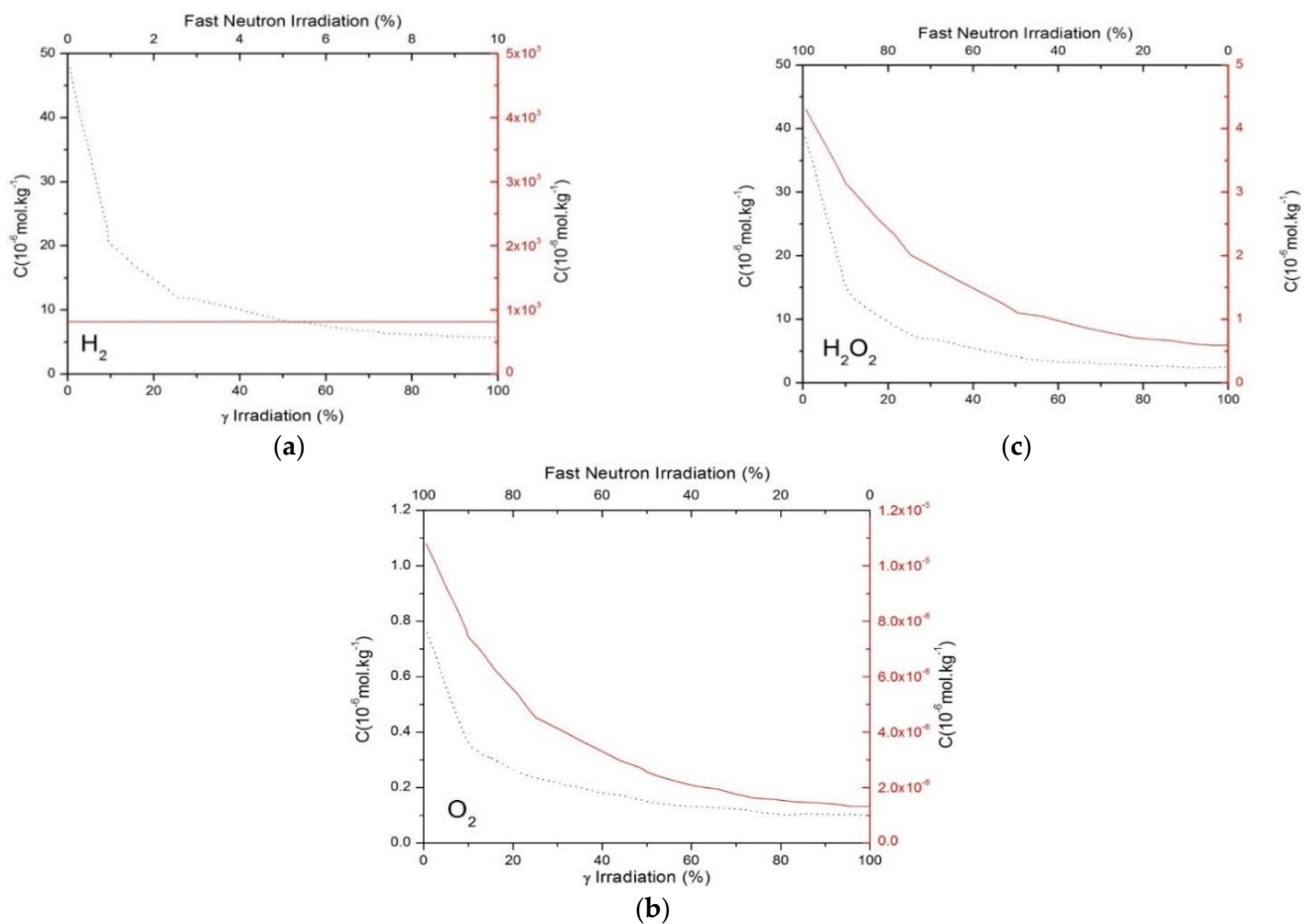


Figure 22. Predicted effect of mixed irradiation (fast neutrons + γ -photon) on the steady-state concentrations of (a) H_2 , (b) O_2 , and (c) H_2O_2 under NWC (.....) and HWC (—) at 250 °C, dose rate = 10 kG/s (after Kritsky et al. [27]). ©2001 ITER Organization. This image is hereby used courtesy of the ITER Organization.

Dose rate is found and predicted to have a significant impact on the yield of radiolysis products, as shown by the data in Figure 23. It is seen that the steady state $[\text{H}_2\text{O}_2] + [\text{O}_2]$ and $[\text{H}_2\text{O}_2]$ increase linearly with the square root of the dose rate; a result that is also predicted by various radiolysis models. Note that this result strictly applies for γ -radiolysis (^{60}Co) of water having an initial oxygen concentration of 0.5×10^{-6} M. Under these conditions, the concentration of oxygen is slightly greater than that of hydrogen peroxide.

The pH of the solution is also predicted in [27] to have a significant effect on radiolysis product yield, as shown in Figure 24. Of particular interest is the maximum in the concentrations of radiolysis products at pH = 11. However, note that the experimental data are only in general agreement with prediction, but that is possibly due to the paucity of experiment. In our opinion, the study performed by Kritsky et al. [27] is a very important milestone in the study of the radiolysis of the coolant in ITER and is possibly the most comprehensive such study published to date. The work of Kritsky et al. [27] provides a solid basis for even more comprehensive analyses of this issue.

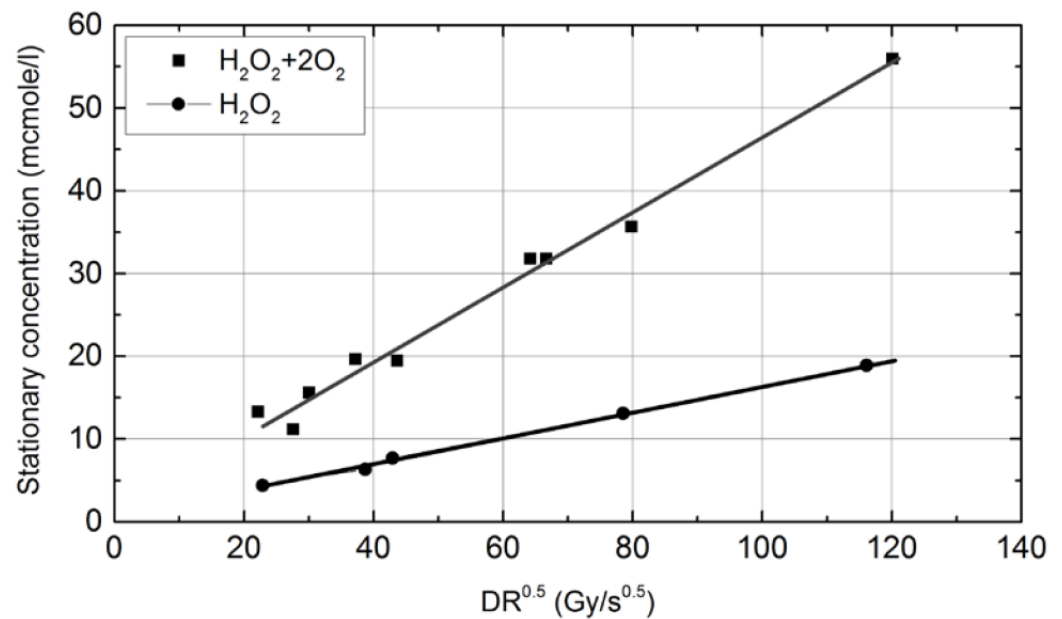


Figure 23. Dependencies of $[H_2O_2] + [O_2]$ and $[H_2O_2]$ on the square root of the dose rate for γ -radiolysis (^{60}Co) of water having an initial oxygen concentration of $0.5 \times 10^{-6} \text{ M}$ (after Kritsky et al. [27]). ©2001 ITER Organization. This image is hereby used courtesy of the ITER Organization.

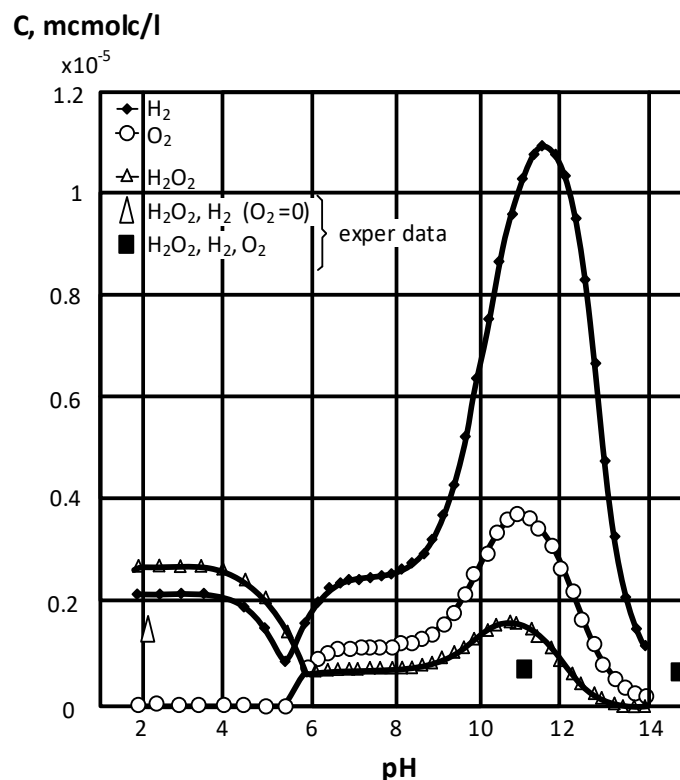


Figure 24. Predicted vs. experimental dependencies of the concentrations of H_2 , O_2 , and H_2O_2 on pH (after Kritsky et al. [27]). ©2001 ITER Organization. This image is hereby used courtesy of the ITER Organization.

The next model to be analyzed is that of Christensen et al. [28], which was used for modeling water radiolysis in the INCA (In-Core Autoclave test) loop at the Studsvik R-2 reactor in Sweden under conditions that simulated the ITER PHTS. The reaction model

employed is like that given in Table 5 for the radiolysis of pure water, except that the model presented in [28] includes iron species and an organic entity (i.e., fulvic acid). Clearly, the same issues identified with the model in Table 4 exist with the model in [28]. The radiolytic yields employed by Christensen et al. [28] are presented in Tables 16 and 17.

Table 16. Summary of primary (?) * radiolytic yields employed by Christensen et al. [28] in modeling radiolysis in the INCA loop.

Reference	t (°C)	e_{aq}^-	H	H ₂	OH	H ₂ O ₂	HO ₂	H ⁻	–H ₂ O
γ									
Ishigure	250	3.54	0.94	0.56	3.48	1.06	0		5.59
	300	3.58	0.92	0.64	4.79	0.50	0		
Elliot	285	3.53	0.90	0.63	4.68	0.50	0		
	250	3.41	0.86	0.60	4.43	0.52	0		
Cohen, Christensen	285	3.36	0.70	0.38	3.52	0.44	0		7.76
Burns	~290	2.7	0.61	0.43	2.86	0.61	0.03	2.7	
Kent	270	3.6	0.68	0.70	5.7	0.28	0		
Selected values	285	3.50	0.90	0.60	4.5	0.55	0	3.5	9.1
Fast neutrons									
Ishigure	250	0.68	0.52	1.52	1.66	1.29			4.24
Elliot	300	0.61	0.34	1.26	2.02	0.65	0.05		
Cohen, Christensen	~290	0.46	0.45	0.91	0.61	0.73	0.22		
Burns	~290	0.93	0.50	0.88	1.09	0.99	0.04	0.93	
	250	0.60	0.34	1.16	2.39	0.33	0.05		
Elliot	300	0.61	0.34	1.21	2.76	0.19	0.05		
Selected values	285	0.65	0.45	1.26	1.77	0.85	0.05	0.65	4.22

* The “?” indicates that it is not clear that the listed G values qualify as “primary” yields; i.e., it is not evident from the original source that they correspond to yields within the spurs at times of <0.01 ns.

Table 17. G-values as a function of temperature for the radiolysis of water due to n and γ irradiation according to Christensen et al. [28].

	25 °C	285 °C	dG/dT	G(S, T) = G (S, 25) + (T – 25) × dG(S)/dT			
				25 °C	50 °C	100 °C	150 °C
Gamma							
e _{aq} [−]	2.65	3.5	3.269 × 10 ^{−3}	2.650	2.732	2.895	3.059
H	0.55	0.9	1.346 × 10 ^{−3}	5.500 × 10 ^{−1}	5.837 × 10 ^{−1}	6.510 × 10 ^{−1}	7.183 × 10 ^{−1}
H ₂	0.45	0.6	5.769 × 10 ^{−4}	4.500 × 10 ^{−1}	4.644 × 10 ^{−1}	4.933 × 10 ^{−1}	5.221 × 10 ^{−1}
OH	2.8	4.5	6.538 × 10 ^{−3}	2.800	2.963	3.290	3.617
H ₂ O ₂	0.65	0.55	−3.846 × 10 ^{−4}	6.500 × 10 ^{−1}	6.404 × 10 ^{−1}	6.212 × 10 ^{−1}	6.019 × 10 ^{−1}
HO ₂	0	0.00	0.000	0.000		0.000	0.000
Neutrons							
e _{aq} [−]	0.5	0.65	5.769 × 10 ^{−4}	5.000 × 10 ^{−1}	5.144 × 10 ^{−1}	5.433 × 10 ^{−1}	5.721 × 10 ^{−1}
H	0.41	0.45	1.538 × 10 ^{−4}	4.100 × 10 ^{−1}	4.138 × 10 ^{−1}	4.215 × 10 ^{−1}	4.292 × 10 ^{−1}
H ₂	1.02	1.26	9.231 × 10 ^{−4}	1.020	1.043	1.089	1.135
OH	0.74	1.77	3.962 × 10 ^{−3}	7.400 × 10 ^{−1}	8.390 × 10 ^{−1}	1.037	1.235
H ₂ O ₂	1.03	0.85	−6.923 × 10 ^{−4}	1.030	1.013	9.781 × 10 ^{−1}	9.435 × 10 ^{−1}
HO ₂	0.05	0.05	0.000	5.000 × 10 ^{−2}	5.000 × 10 ^{−2}	5.000 × 10 ^{−2}	5.000 × 10 ^{−2}

Note: The original table gives values at temperatures up to 300 °C.

Although the G-values are reasonably consistent from one source to another, in the authors’ opinion, the agreement is somewhat illusory because G-values all appear to come from four sources: Burns and Moore [44,45,264,265,275]; Buxton [36,43,63,67,80,125,132,137,148,177,178,197]; Ershov [72], Katsumara, et al. [83], and Elliot [47,48,52,53,55,60,62–64,80–82,89,108,126,128,132,135–137,159], with minor variations for (in the authors’ opinion) untraceable reasons. This same level of skepticism concerning the radiolytic yields has been expressed in [66,78,113,114,151]. Again, the G-values do not appear to correspond

solely to the desired “primary” (i.e., sub-nanosecond) values but include values for H_2O_2 and HO_2 , for example, that appear to largely form via reactions outside the spur over a much longer time scale, although some formation of these species may occur within the spur. Another demonstration of the suppression of water radiolysis is found in [28], as shown in Figure 25, for systems with and without added hydrogen. Thus, the addition of $5 \text{ cm}^3(\text{STP})/\text{kg H}_2\text{O}$ (0.45 ppm) of hydrogen to the core inlet water of Studsvik’s INCA loop simulating conditions that are expected to exist in the IBED PHTS of ITER leads to the reduction of $[\text{O}_2]$ and $[\text{H}_2\text{O}_2]$ by more than two orders in magnitude. This “suppression of radiolysis” is further illustrated in Figures 26 and 27, where the equivalent oxidizer concentration, $[\text{H}_2\text{O}_2 + \frac{1}{2}\text{O}_2]$, and the ECP are presented as a function of added hydrogen at temperatures of 50°C and 150°C , respectively. At both temperatures, suppression of radiolysis was achieved by the addition of about $1 \times 10^{-4} \text{ M}$ (200 ppb) of hydrogen to the reactor inlet water; this result is in reasonable concert with the findings for BWRs (c.f., Figures 17 and 18), recognizing that the amount of hydrogen required to suppress radiolysis appears to decrease with increasing temperature.

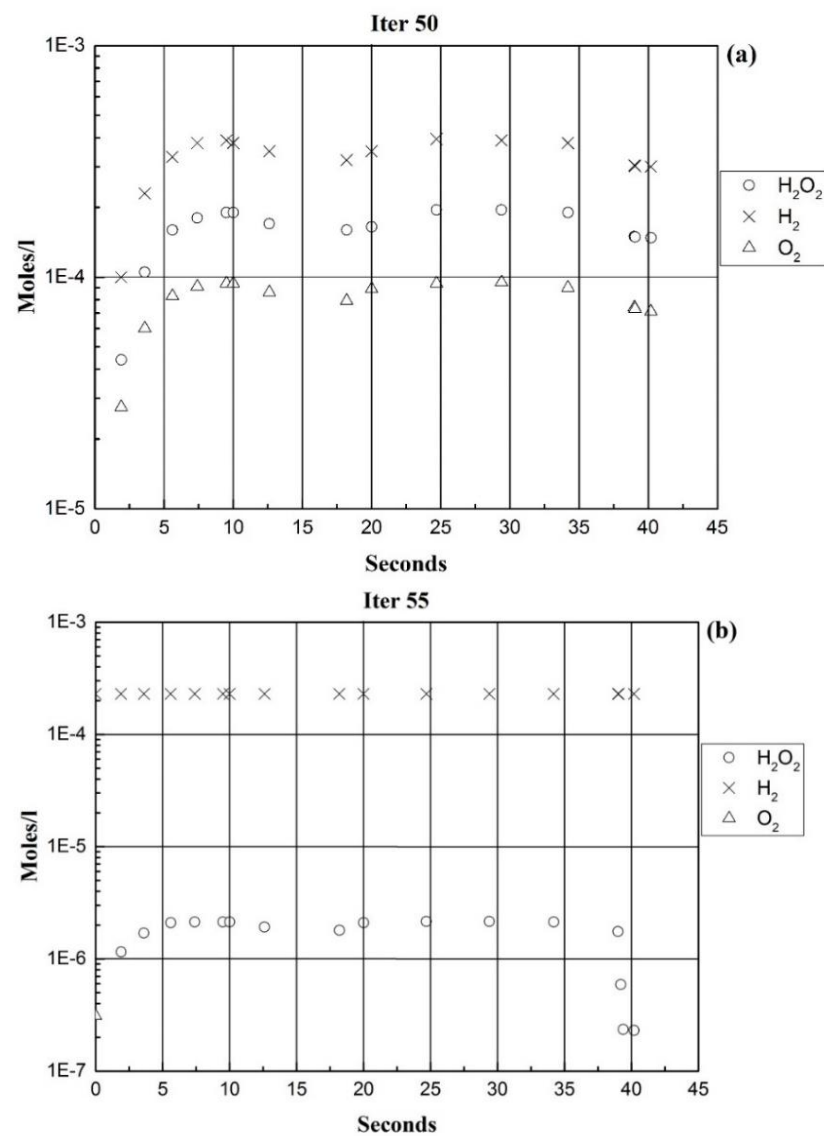


Figure 25. Radiolysis of water in the Studsvik INCA loop at 50°C , with (a) no added hydrogen and (b) $5 \text{ cm}^3(\text{STP})/\text{kg H}_2\text{O}$ (after Christensen et al. [28]). ©1996 ITER Organization. This image is hereby used courtesy of the ITER Organization.

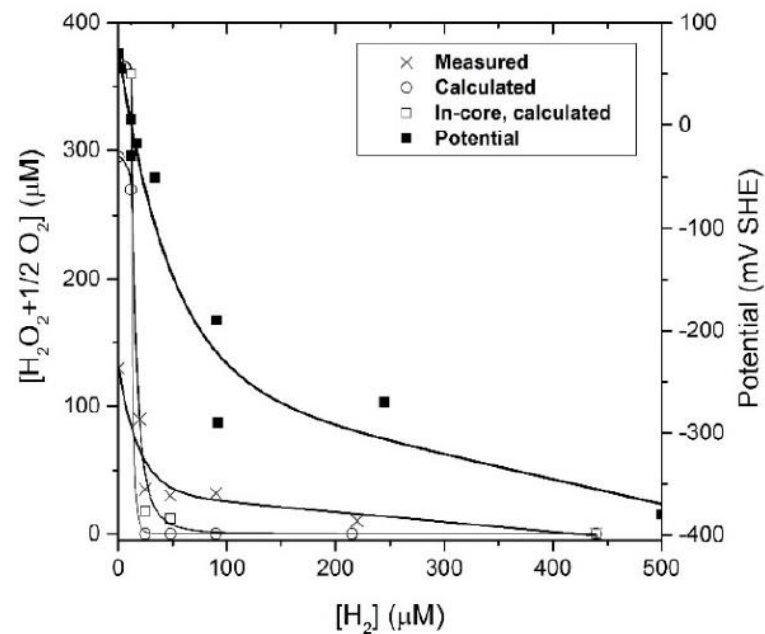


Figure 26. Oxidant concentration and the ECP of stainless steel at 50 °C, as a function of inlet hydrogen concentration as measured in Studsvik's INCA in-reactor loop (after Christensen et.al. [28]). ©1996 ITER Organization. This image is hereby used courtesy of the ITER Organization.

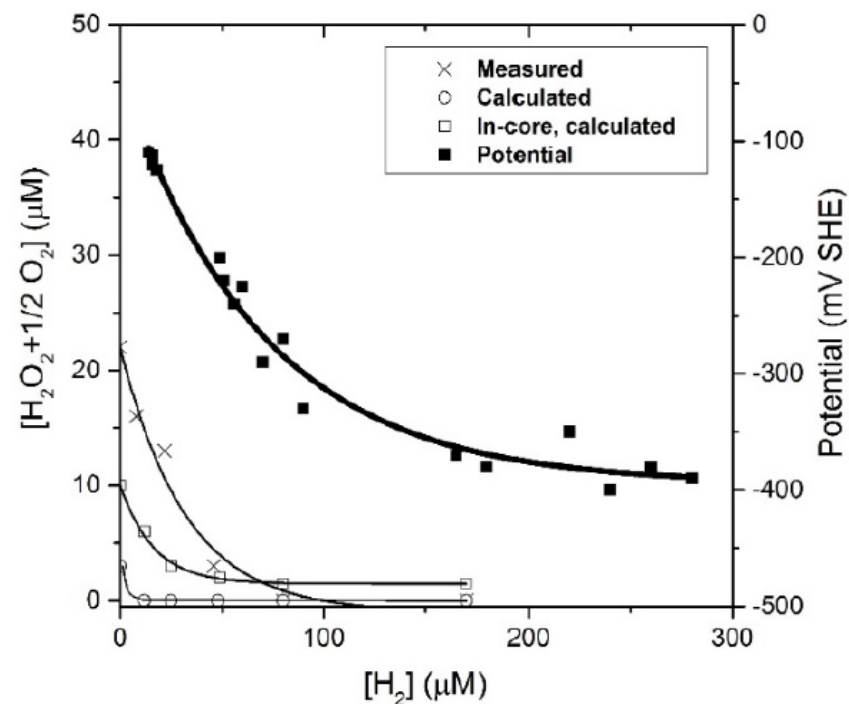


Figure 27. Oxidant concentration and the ECP of stainless steel at 150 °C, as a function of inlet hydrogen concentration as measured in Studsvik's INCA in-reactor loop (after Christensen et.al. [28]). ©1996 ITER Organization. This image is hereby used courtesy of the ITER Organization.

Amongst the most comprehensive radiolysis modeling of ITER is that reported by Elliot and McCracken at the Chalk River Laboratory of Atomic Energy of Canada Ltd. [52,53]. Their work emphasizes modeling of the aqueous LiOH, tritium breeding blanket, rather than the PHTS, but the modeling process is the same, and for that reason the work is included here.

An important issue discussed in [48,53] is the dependence of the radiolytic yields (G-values) on LET (Figure 28), as was also emphasized in [27,168,188,198,200,203]. Generally speaking, those primary radiolysis products that form via the fragmentation of water in the ionization track (e_{aq}^- , H, and OH) decrease with increasing LET (Figure 28), whereas those products that form via reactions within the track (H_2 , H_2O_2 , and HO_2) increase with LET; relationships that have been previously noted in [1]. These trends probably reflect the increasing importance of in situ reactions with increasing LET within the track between the products produced via the fragmentation of water. The fast neutrons produced by the plasma (14.1 MeV), compared with the thermalized neutrons produced in a water cooled/moderated fission reactor, result in a high LET, and the values adopted by Elliot and McCracken [48,53] are those that are given in Figure 28 [53].

The reaction model proposed in [48,53] is considerably more complex than those proposed by others, comprising some 84 reactions, and including irradiation induced by alpha particles and tritons, in addition to that caused by γ -photons and neutrons. The alpha particles and tritons are produced by the fission of 6Li_3 , ${}^6Li_3 + {}^1n_0 \rightarrow {}^3H_1 + {}^4He_2$, as discussed above, which is used to breed tritium. Acid/base dissociation reactions and some ionization reactions (e.g., $H \leftrightarrow H^+ + e_{aq}^-$) are included in the model. Nevertheless, the model also includes reactions between species of like charge, which are of doubtful validity for the reasons discussed previously in this review. Again, as with all radiolysis models, the model proposed in [48,53] appears to be massively underdetermined (i.e., there are many more unknown parameters than there are observations), although it is difficult to be unequivocal on that point because their publications [48,53] possibly do not include the calibrating data for all reactions. This point needs to be carefully assessed in any future study of water radiolysis. Finally, as noted above, the model proposed in [48,53] was used to simulate the chemistry of the aqueous LiOH tritium-breeding blanket, not the PHTS, which will not contain lithium (unless a PWR primary water chemistry is adopted). As such, the ion recoil products 4He_2 and 3T_1 are included, and, assuming their absence, the radiolysis that they cause can be ignored in development of the ITER PHTS radiolysis model. The complexity of the model, as reflected by the number of reactions contained therein, is an important computational issue because the execution time scales roughly with the square of the number of reactions. This becomes a particularly important problem when it is necessary to model the radiolysis of water at closely spaced locations around the entire coolant circuit, as is done for BWRs and PWRs [221]. In those studies, it was necessary to perform several thousand executions of the code to effectively model the radiolysis, ECP, and crack growth behavior of the system while maintaining the total execution time to 30 min or less. This should also be the goal in development of the ITER PHTS radiolysis model.

In Part II of this review, selected radiolysis data are used to predict the ECP and the CGR of a standard crack (0.5 cm in length loaded to a stress intensity factor $K_I = 25.0 \text{ MPa}\cdot\text{m}^{1/2}$) so as to ascertain the likely impact of coolant chemistry on the susceptibility of RHTS components fabricated from Type 304 SS to IGSCC.

To estimate corrosion damage at any point of the coolant circuit, the concentrations of all species at any point in the loop as a function of time are required. Such information can be obtained by solving the equations of mass balance for all species, if the fluid conditions (e.g., temperature, radiation dose rate, hydrodynamics) are known at every point in the loop. Examples of such calculations can be found in [1,35,216]. For the analysis of the ITER IBED PHTS, the circuit can be subdivided into modules and blocks, and within each block, the known geometrical parameters (i.e., volume, length, diameter) and environmental conditions (i.e., temperature, flow rate, γ -photon and neutron energy deposition rates) are deemed to be constant during the burn and dwell periods. The entire IBED PHTS is represented as a series of combinations of these blocks, by analogy with electric circuits. Each independent series of block combinations is called a "module." Within each module, the mass flow rate is constant. The IBED PHTS in the Plasma Flux Area (subject to intense gamma and neutron radiation) comprises 12 independent modules, each containing from

1 to 19 blocks. Simulated IBED PHTS components that are Out-of-Flux Area (OPFA, outside of the radiation area) include distribution and connection piping, heat exchangers, pumps, and headers. The scheme of configuration of all modules is available in [1,35].

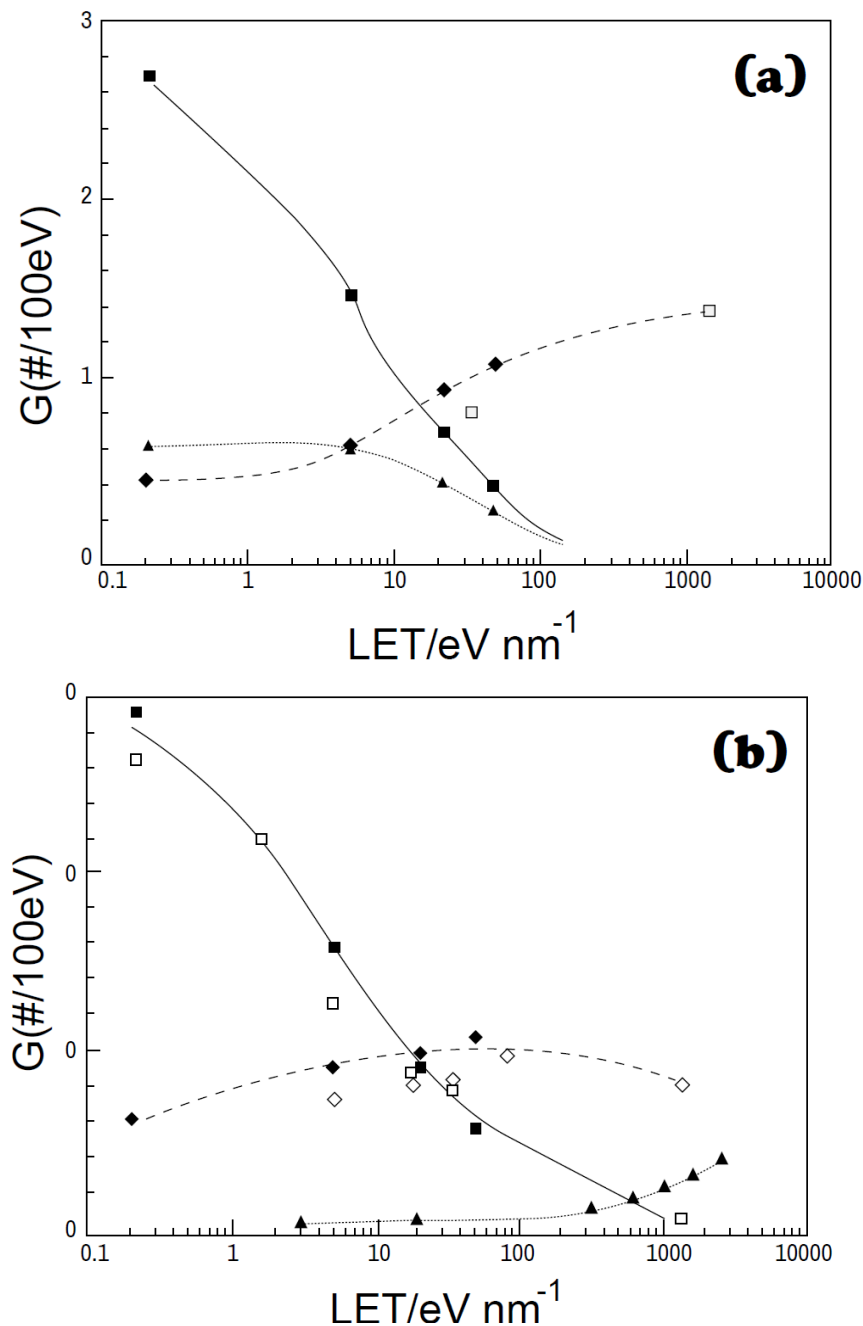


Figure 28. (a) G-values for e_{aq}^- (filled squares), H (filled triangles) and H₂ (filled and open diamonds) as a function of LET. (b) G-values for OH (filled and open squares, H₂O₂ (filled and open diamonds) and HO₂ (filled triangle) (filled squares), as a function of LET (data from Elliot and McCracken [53]).

In each block, the following parameters are characterized: cross section area, A (m²); length, L (m); water volume, V (m³); coolant mass flow rate, U (kg/s); average water temperature, T_{av} (°C); and the gamma and neutron energy deposition rates, Q_γ and Q_n , respectively (W/cm³). The average hydrodynamic velocity in the block is calculated as $v = (U/\rho)/A$ (m/s), where ρ is density of water, (g/cm³). Residential time for each species in the block is calculated as $t_L = L/v$ (s), i.e., this is the time for any species to move through the block (from the input to the output of the block). In calculations for multiple cycles

of the coolant in the entire IBED PHTS system, it is assumed that the concentrations of species at the inlet of each block for the current cycle were equal to the concentrations of the species at the end of the Out-of-Plasma-Flux Area (OPFA) for the previous cycle. The transit time in the OPFA is important because it is during this time and in the absence of energy deposition from the intense gamma and neutron radiation that the radiolytic species recombine, resulting in a decrease in their concentrations.

The system of mass transfer equations for each block was solved by using the following approximations.

- The one-dimensional approximation can be applied. That is, all quantities can be represented as a function of a single spatial coordinate—the distance down the block (tube), x . This means that all quantities to be averaged either differ insignificantly from the average value or undergo a substantial change within a narrow region next to the tube surface. For the present conditions, the impact of the boundary region on the average concentration in the bulk coolant is found to be negligible because of the overwhelming (homogeneous reaction) radiolytic source of radiolysis products.
- Along the direction, x , all species are transported by convection only. Therefore, diffusion and migration are neglected in comparison with the relatively large convective transfer. This condition is valid for the high flow rates that are envisioned for the IBED PHTS.
- The geometry of each tube does not depend on the coordinate, x , (i.e., the area, A , and the wetted perimeter, P , are constants within a block). It is assumed that the density of the liquid (i.e., water) does not change substantially in the tube; therefore, $U(t)$ is only a function of time and not of position.
- The influence of the heterogeneous reactions (i.e., chemical, and electrochemical) is not taken into consideration, i.e., only changes of species concentrations due to the radiation and homogeneous chemical reaction are considered.

It can be shown [1,35] that after all of the above simplifications are adopted, the system of transport equations can be reduced to the set of the first order ordinary equations:

$$\frac{dC_k}{dt} = \delta G_{\gamma k} Q_{\gamma} + \delta G_{nk} Q_n + \sum_m \mu_{mk} k_m \prod_k C_k^{\nu_{mk}} - \sum_m \nu_{mk} k_m \prod_k C_k^{\mu_{mk}}, \quad k = 1, 2, \dots, N \quad (9)$$

with the boundary conditions:

$$C_k = C_{k0} \text{ at } t = 0 \quad (10)$$

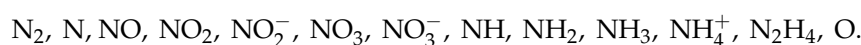
describing the concentrations of all species, C_k , as a function of the retention time inside any particular block. Here, C_{k0} is the concentration of species k (mol/L) at the block inlet (which correspond retention time $t = 0$), N is the total number of species in the solution. Note that, for $t > t_L$, the concentrations do not depend on the initial values (all liquid that was initially in the block for $t > t_L$ is now out of the block). Because $t_L \ll t_c$, it is not necessary to take into account the initial conditions (see second paragraph below). The first two terms in the right side correspond to the primary dose irradiation, where Q_{γ} and Q_n are the energy deposition rates by γ -photon and neutron radiation (W/cm^3), respectively; $G_{\gamma k}$ and G_{nk} are the corresponding gamma and neutron primary G-values for the species k (no./100 eV), respectively; and δ is the conversion factor. The second two terms in the right side correspond to the homogeneous chemical reactions that are described by the set of M chemical reactions with the stoichiometry:

$$\sum_k \mu_{mk} C_k \rightarrow \sum_k \nu_{mk} C_k, \quad m = 1, 2, \dots, M. \quad (11)$$

where μ_{mk} and ν_{mk} are the stoichiometric coefficients of the compound (or element) k in module m , and k_m is the reaction rate constant. Note that Equation (9) does not include a term for the transfer of a volatile species (e.g., H_2) to a gas phase, as is the case for a BWR [216], because no boiling of the coolant occurs in the ITER.

Equation (9) with initial conditions (10) describes mass transfer inside the block only in the region $x < \int_0^t V(t')dt'$ (or in the region $x < Vt$ for $V = \text{const}$). However, assuming that during any operational cycle of duration t_c the velocity through each block does not change and that t_c is much greater than the residence time, t , the conclusion is made that the equations presented above can be used to describe mass transfer at any point in the block at any moment of time.

It is assumed that 11 species listed in Table 9 are generated as a result of water radiolysis, although not all of the species may be formed within the spurs at a time period of less than 0.01 ns. The presence of these metal ions— Cu^+ , Cu^{2+} , Fe^{2+} , Fe^{3+} —in the solution [27,28] is also considered; these ions may act as homogeneous catalysts for some of the reactions in the radiolysis model presented in [1,35]. In addition, it is assumed that, because of the influence of radiation on N_2 molecules and due to the generation of nitrogen species via the nuclear reactions $^{16}\text{O}_8(^1n_0, ^1p_1)^{16}\text{N}_7$ and $^{17}\text{O}_8(^1n_0, ^1p_1)^{17}\text{N}_7$ with the oxygen isotopes in water, the following species are present in the solution [271]:



The G-values were obtained by the procedure described in the paragraph below Equation (8). The values shown in Tables 18 and 19 are used in the IBED PHTS radiolysis model.

Table 18. Improved G-values (no./100 eV) for low LET (e.g., γ -photon) radiation at different temperatures (based on data from [60]).

Species	25 °C	70 °C	100 °C	130 °C	150 °C	250 °C
e_{aq}^-	2.759	2.985	3.136	3.278	3.364	3.597
H	0.58	0.6	0.61	0.627	0.646	0.937
OH	2.798	3.248	3.533	3.814	4.001	5.005
H^+	2.759	2.985	3.136	3.278	3.364	3.597
OH^-	0	0	0	0	0	0
O_2	0	0	0	0	0	0
O_2^-	0	0	0	0	0	0
H_2	0.439	0.465	0.477	0.488	0.497	0.575
H_2O_2	0.709	0.633	0.583	0.534	0.501	0.339
HO_2^-	0	0	0	0	0	0
HO_2	0	0	0	0	0	0

Table 19. Improved G-values (no./100 eV) for high-energy neutrons (14 MeV) at different temperatures (based on data from [25]).

Species	25 °C	70 °C	100 °C	130 °C	150 °C	250 °C
e_{aq}^-	1.031	1.048	1.06	1.071	1.079	1.116
H	0.506	0.506	0.507	0.507	0.507	0.508
OH	1.18	1.515	1.738	1.961	2.109	2.849
H^+	1.059	1.076	1.087	1.099	1.106	1.144
OH^-	0	0	0	0	0	0
O_2	0	0	0	0	0	0
O_2^-	0.028	0.028	0.027	0.027	0.027	0.027
H_2	0.803	0.842	0.868	0.893	0.911	0.997
H_2O_2	0.837	0.717	0.638	0.558	0.505	0.241
HO_2^-	0	0	0	0	0	0
HO_2	0.05	0.05	0.05	0.05	0.05	0.05

The G-values for temperatures in-between tabulated values were calculated by Lagrange interpolation. Comparison shows that there is good agreement between the improved and original G-values (the discrepancy is within 1.5%). However, the improved G-values exactly satisfy the laws of mass and charge conservation.

For water radiolysis, the rate constants proposed in [21] are used. For reactions involving metal ions, the data from [27] (Cu ions) and [28] (Fe ions) are employed. For reactions containing nitrogen atoms and atomic oxygen, O, the data (including G-values) proposed in [271] are employed (if N₂ is decomposed under radiation to generate nitrogen atoms). The dependence of the rates of the reactions on temperature is described by the usual Arrhenius relation, but in some cases this dependence is obtained by interpolation of the experimental data. The complete list of the rates of all 89 reactions included into the consideration at temperature range between 25 °C and 250 °C is provided in [1]. The values of the rate constants for temperatures in-between the tabulated values are calculated by Lagrange interpolation.

A modularization of the IBED PHTS of the ITER for radiolysis assessment is presented in Figure 29. Each module inside the Plasma Flux Area (PFA) is yellow-colored and contains the indicated number of blocks in series. The number of modules and associated blocks in the IBED PHTS is provided in Table 20. Each module with its component blocks in the PFA is located inside the Vacuum Vessel and absorbs heat from the plasma via the flowing coolant.

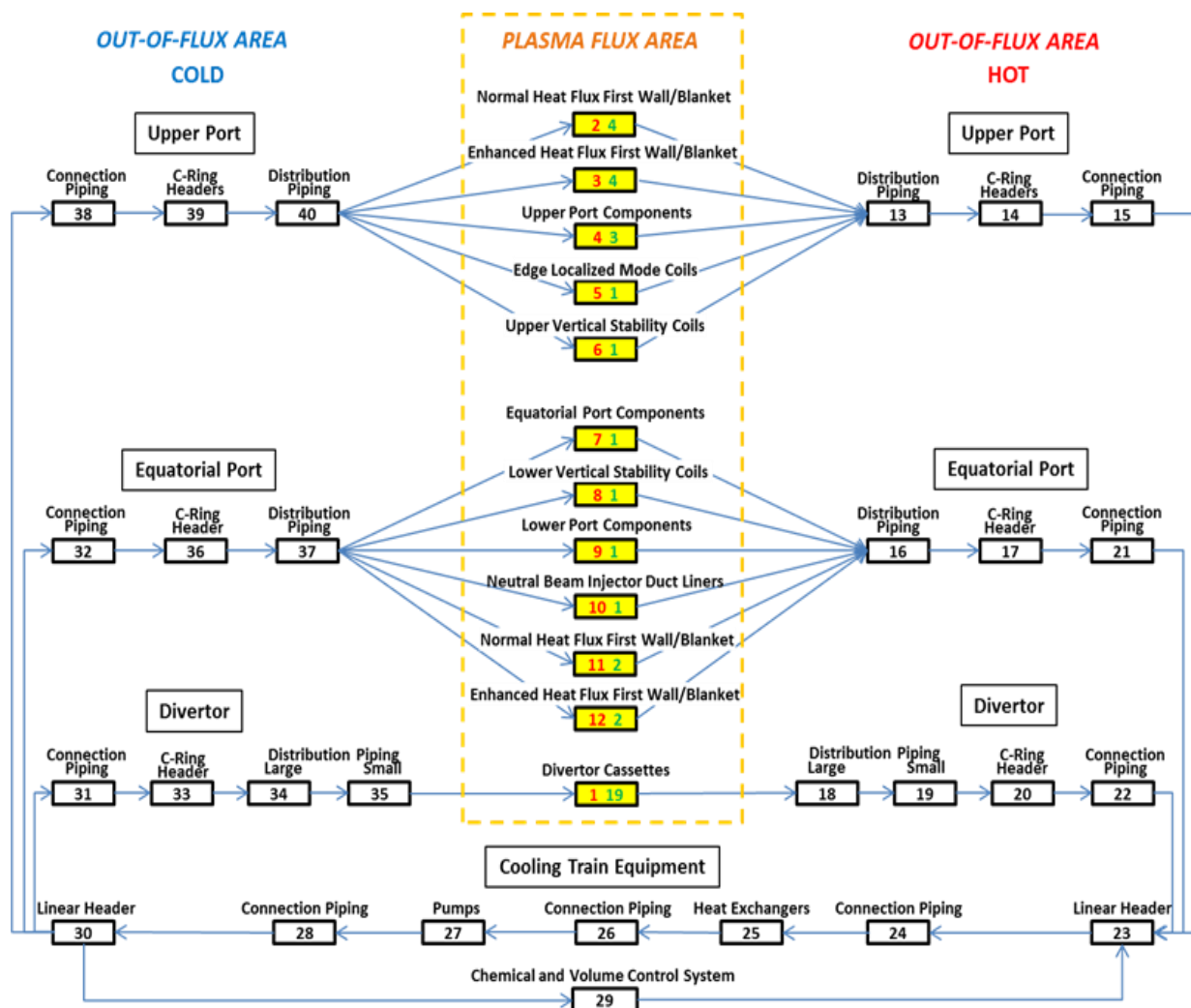


Figure 29. Modularization of the IBED PHTS of the ITER for Radiolysis Assessment [1]. ©2017 OLI Systems, Inc.

Table 20. List of IBED PHTS Modules for Radiolysis Simulation [1,35].

Modules	Number of Blocks	Components
		Plasma Flux Area (PFA)
Module 1	19	Divertor
Module 2	4	Normal Heat Flux First Wall/Blanket
Module 3	4	Enhanced Heat Flux First Wall/Blanket
Module 4	3	Upper Ports
Module 5	1	Edge Localized Mode Coils
Module 6	1	Upper Vertical Stability Coils
Module 7	1	Equatorial Port Components
Module 8	1	Lower Vertical Stability Coils
Module 9	1	Lower Port Components
Module 10	1	Neutral Beam Injectors Duct Liners
Module 11	2	Normal Heat Flux First Wall/Blanket
Module 12	2	Enhanced Heat Flux First Wall/Blanket
		Out-of-Plasma-Flux Area (OPFA)
Module 13	1	Upper Pipe Chase Distribution Piping [Hot]
Module 14	1	Upper Pipe Chase C-Shaped Ring Headers (C-Ring Headers) [Hot]
Module 15	1	Connection Piping between Upper Pipe Chase C-Ring and Linear Headers [Hot]
Module 16	1	Equatorial Port Distribution Piping [Hot]
Module 17	1	Equatorial Port C-Ring Header [Hot]
Module 18	1	Divertor Small Distribution Piping [Hot]
Module 19	1	Divertor Large Distribution Piping [Hot]
Module 20	1	Divertor C-Ring Header [Hot]
Module 21	1	Connection Piping between Equatorial Port C-Ring and Linear Headers [Hot]
Module 22	1	Connection Piping between Divertor C-Ring and Linear Headers [Hot]
Module 23	1	Linear Header [Hot]
Module 24	1	Connection Piping between Linear Header and Heat Exchangers
Module 25	1	Heat Exchangers
Module 26	1	Connection Piping between Heat Exchangers and Pumps
Module 27	1	Pumps
Module 28	1	Connection Piping between Pumps and Linear Header [Cold]
Module 29	1	Chemical and Volume Control System
Module 30	1	Linear Header [Cold]
Module 31	1	Connection Piping between Linear and Divertor C-Ring Headers [Cold]
Module 32	1	Connection Piping between Linear and Equatorial Port C-Ring Headers [Cold]
Module 33	1	Divertor C-Ring Header [Cold]
Module 34	1	Divertor Large Distribution Piping [Cold]
Module 35	1	Divertor Small Distribution Piping [Cold]
Module 36	1	Equatorial Port C-Ring Header [Cold]
Module 37	1	Equatorial Port Distribution Piping [Cold]
Module 38	1	Connection Piping between Linear and Upper Pipe Chase C-Ring Headers [Cold]
Module 39	1	Upper Pipe Chase C-Ring Headers [Cold]
Module 40	1	Upper Pipe Chase Distribution Piping [Cold]

As seen, the system comprises three principal areas: the PFA is subjected to intense neutron and γ -photon irradiation during the plasma burn period (550 s, including ramp-up and ramp-down, Figure 9) and Out-of-Plasma Flux Area (OPFA) which is subdivided into Hot OPFA with temperature 126 °C (upstream of heat exchangers) and Cold OPFA with temperature 70 °C (downstream of the heat exchangers). The OPFA is not subjected

to irradiation. For the analysis, the IBED PHTS can be subdivided into modules and blocks and is represented as a series of combinations of these blocks. Each independent series of block combinations is called a “module.” The IBED PHTS in the PFA consists of 12 independent modules, each containing from 1 to 19 blocks. For example, the Divertor Cassettes comprises one module that contains nineteen blocks [1,35]. Simulated IBED PHTS components that are OPFA include distribution and connection piping, heat exchangers, pumps, and headers. These are represented by 28 modules. Table 20 lists the modules associated with the PFA and the OPFA, with number of blocks in each module.

As is common practice, this system can be schematically represented as comprising two parts, PFA (red) and OPFA (yellow), as shown in Figure 30 [1,35].

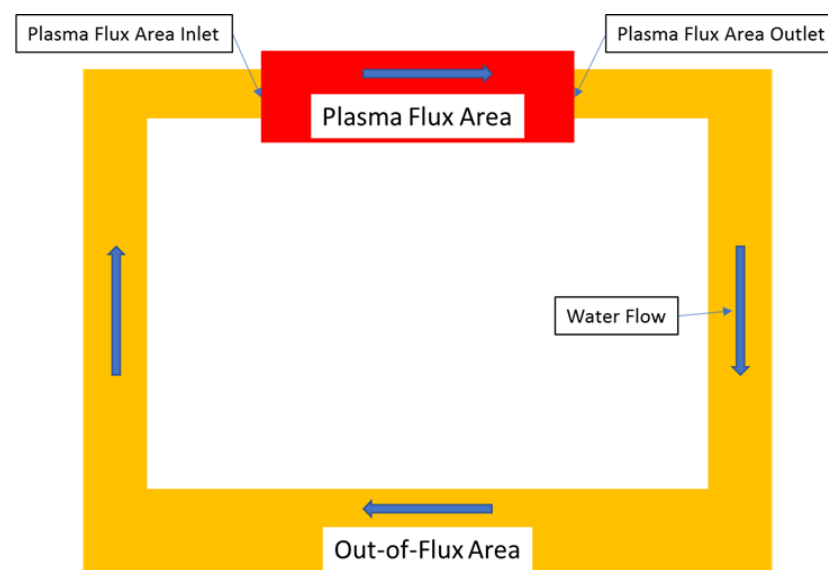


Figure 30. Simplified representation of the IBED PHTS.

The module chosen to model represents 15 Equatorial Ports, which experience the highest energy deposition rates (Q_n and Q_γ of 3.2 and 4.3 W/cm³, respectively). The actual data employed in the model are summarized in Table 21, which also contains specified limits on the concentrations of metal ions, oxygen, and added hydrogen. The temperature of 98 °C is the average of the temperatures at the module inlet (70 °C) and the module outlet (126 °C).

Table 21. Set of parameters for the simplified model representing a single module in the radiolysis assessment.

Parameter	Value
Hydrogen, cc(STP)/kg	1
Oxygen, ppb	10
Cu ²⁺ , ppb	10
Cu ⁺ , ppb	0
Fe ²⁺ , ppb	10
Fe ³⁺ , ppb	0
N ₂ , ppm	2
Temperature, °C	98
t_L , s	81.3
Q_n , W/cm ³	3.2
Q_γ , W/cm ³	4.3

The chosen module may be compared with some other modules in the cooling system; an example is summarized in Table 22. Thus, the chosen model is predicted to have the

highest radiation energy deposition rates (3.2 and 4.3 W/cm³ for neutrons and γ -photons, respectively, for a total energy deposition rate of 7.5 W/cm³) and hence are expected to display the greatest impact of radiolysis on the chemistry and electrochemistry of the coolant. As shown in Table 22, these other modules also differ significantly in terms of residence time, mass flow rate, and volume, even though the temperatures are predicted to be the same, because they draw on the same source of coolant which flows through regions of similar heat flux. By way of comparison, a typical BWR has an in-core energy deposition rate of 50–60 W/cm³ suggesting that the radiolytic environment in the ITER will be somewhat muted compared with that in a fission BWR.

Table 22. Simulated thermohydraulic and energy deposition rate data for 15 Equatorial Ports (Module 7 contains 1 block), 2 Lower Vertical Stability Coils (Module 8 contains 1 block), 3 Lower Ports (Module 9 contains 1 block), and 3 NBI Duct Liners (Module 10 contains 1 block). Further details of these components are given in Refs. [1,35].

Parameter	15 Equatorial Ports	2 Lower Vertical Stability Coils	3 Lower Ports	3 NBI Duct Liners
T_c , °C	98	98	98	98
t_L , s	81.3	35.6	192.3	10.6
Q_n , W/cm ³	3.2	0.187	10 ^{−6}	0.2
Q_γ , W/cm ³	4.3	0.033	10 ^{−6}	0.8

By performing radiolysis assessment of the entire IBED PHTS, the emphasis is on the accumulation of hydrogen, oxygen, and hydrogen peroxide because these species dominate the ECP and hence the corrosion behavior and the crack growth rate in a structural material. As noted above, for assessing the behavior of the radiolysis species in the entire IBED PHTS module, this system can be schematically represented by the simplified model shown in Figure 30 [1,35].

Figures 31–33 illustrate results of the model calculations in a typical Equatorial Port module with a high energy deposition rate as a function of the concentration of added hydrogen. The values of the concentrations of species at the module inlet, temperature, energy deposition rates inside the module, and retention time, are given in Table 20. Figure 31 shows that the system rapidly reaches a steady state after the initiation of irradiation as the coolant enters the PFA. In fact, all the concentrations of all radiolysis products are predicted to be constant after irradiation for 10 ms with that of HO₂ showing some small change up to 100 ms (Figure 31). This time is short compared with the residence time (tens of seconds) and hence the concentrations can be assumed to be constant throughout the PFA and the OPFA. Therefore, because the wall material, temperature, and hydrodynamic velocity inside the module remain unchanged during virtually entire retention time, we assume that the ECP does not change within each area of the module; i.e., the corrosion conditions inside each area of the module can be characterized by the single ECP value.

Figure 32 shows that addition of [H₂] = 1 cc (STP)/kg H₂O (0.09 ppm) reduces the concentration of oxygen to a level that is significantly lower than the target value (10 ppb = 3.3×10^{-7} m). However, the concentration of oxygen increases above the target value if the concentration of hydrogen decreases to below 0.2 cc (STP)/kg H₂O (18 ppb). At the same time, the concentration of hydrogen peroxide increases to a level that is substantial from a corrosion viewpoint, although the steady-state value is predicted to decrease with increasing hydrogen (see Figure 33). To our knowledge, no specification has been placed on the concentration of H₂O₂, which we find surprising because hydrogen peroxide is a much stronger oxidizing agent than is oxygen on a per-mole basis, as reflected in their standard reduction potentials of 1.77 V_{she} and 1.23 V_{she}, respectively. Accordingly, H₂O₂ is much more aggressive towards general and localized corrosion phenomena than is O₂. We argue in Part II [291] that the prudent approach to managing water chemistry in the mitigation of

corrosion would be to place a limit on the electrochemical corrosion potential (ECP), as has been done in the operation of BWRs.

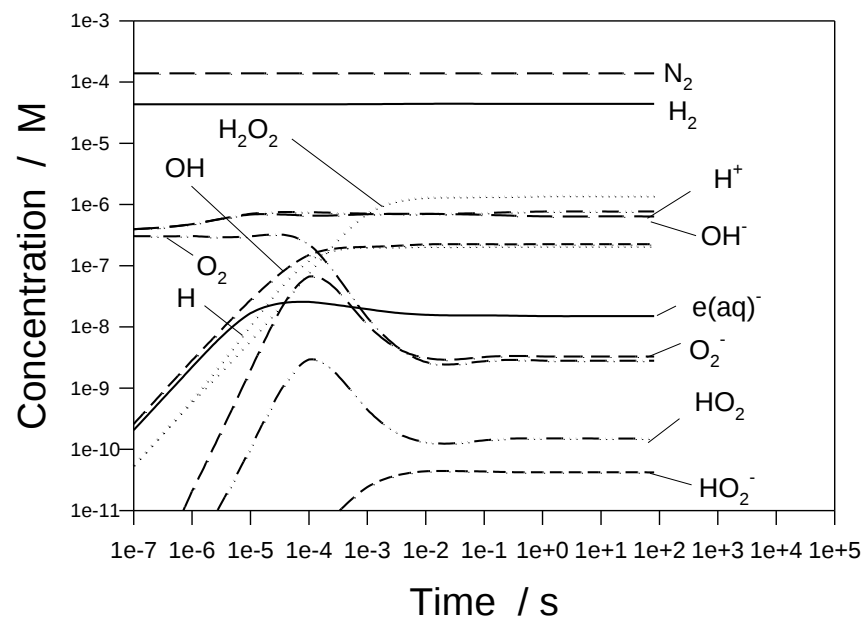


Figure 31. Predicted concentrations of radiolysis species in the single modeled module (see Table 20) as a function of time with addition of 1 cc (STP)/kg H₂O of hydrogen.

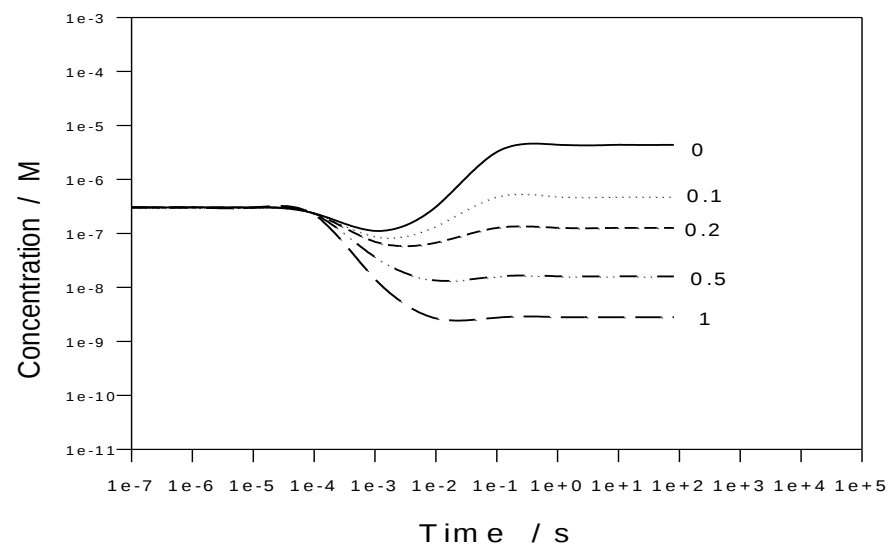


Figure 32. Predicted concentration of oxygen in the single modeled module as a function of time for different initial concentrations of hydrogen in cc (STP)/kg H₂O.

The concentration of molecular nitrogen practically does not change (Figure 31), indicating that bond fissioning of N₂ to form reactive atomic nitrogen is not extensive. In accordance with [26], the maximum concentrations of nitrogen isotopes derived from the nuclear reactions (¹⁶N₇ and ¹⁷N₇) are equal to 4×10^{-10} M and 3.0×10^{-14} M, respectively. Therefore, the concentrations of all species containing nitrogen are very low and do not represent a significant source of radiolysis products, although they may pose a radiation hazard, as is the case for BWRs operating on hydrogen water chemistry where the nitrogen isotopes (¹⁶N₇ and ¹⁷N₇) exist in the form of volatile NH₃, which is transferred to the steam phase by in-core boiling and then swept into the turbine hall that was not (originally) designed as a radiation area. This required installation of extensive shielding, including

the strengthening of structures, to achieve acceptable man REM (Rontgen Equivalent Man) costs.

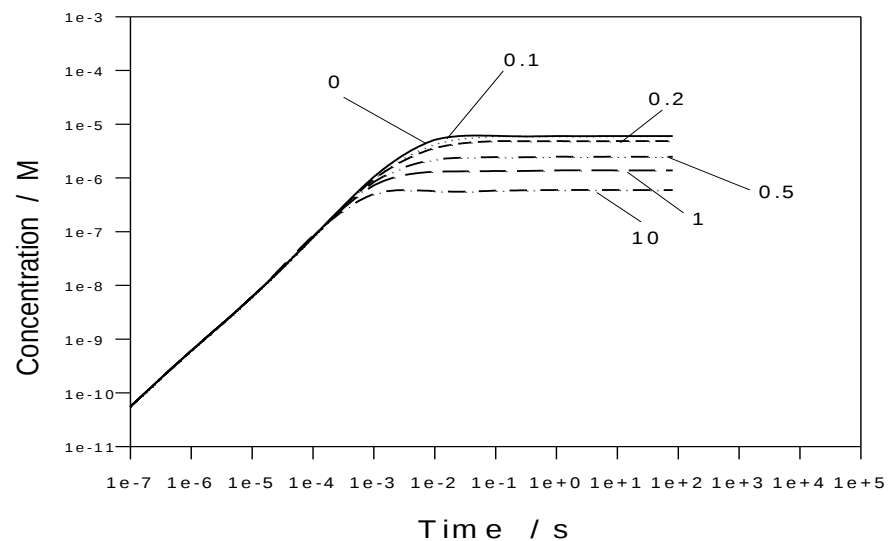


Figure 33. Predicted concentration of hydrogen peroxide in the single modeled module as a function of time for different initial concentrations of hydrogen in cc (STP)/kg H₂O.

Figure 34 shows predicted concentrations of metal-containing species as a function of time, assuming initial conditions are $[\text{Cu}^{2+}] = 10$ ppb, $[\text{Fe}^{2+}] = 10$ ppb, and $[\text{Cu}^+] = [\text{Fe}^{3+}] = 0$ [1,35]. Because of the presence of added hydrogen [1 cc(STP)/kg H₂O], the most highly oxidized species (Cu^{2+} , Fe^{3+}) tend to be reduced to Cu^+ , Fe^{2+} , respectively, as the system achieves a steady state. The final concentrations reflect the redox potential of the coolant ($E_{O/R}$), which is analogous to the ECP, except the metal substrate is inert (and hence is measured using a Pt indicator electrode). The more negative the value of $E_{O/R}$, the more reducing is the environment and, hence, the greater is the driving force for the reduction of species to lower oxidation states. Figure 35 shows concentrations of metal-containing species for initial conditions of $[\text{Cu}^+] = 10$ ppb, $[\text{Fe}^{3+}] = 10$ ppb, and $[\text{Cu}^{2+}] = [\text{Fe}^{2+}] = 0$ [1,35]. Note that the calculations displayed in Figures 34 and 35 differ in the initial concentrations of the metal species. Again, the hydrogen addition results in the reduction of Cu^{2+} and Fe^{3+} to Cu^+ , and Fe^{2+} , respectively. These findings have important consequences with respect to the corrosion of structural materials in the IBED PHTS. For example, a lower concentration of Cu^{2+} reduces the rate of the cathodic reaction $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$. An important issue that does not appear to have been explored is whether metallic copper could be plated out on the structural alloy surfaces. If that occurs, the Cu nuclei may act as nucleation sites for passivity breakdown and localized (pitting) corrosion, a phenomenon that is well documented for stainless steels.

As noted above, in performing radiolysis assessment of the entire IBED PHTS, the emphasis is on the accumulation of hydrogen, oxygen, and hydrogen peroxide because these species dominate the ECP and hence the crack growth rate in a structural material. Instead of a detailed description of the mass transfer of species out of the radiation blocks at all downstream positions, the following approximation is used [1,35]. The average concentration of each specie, C_k , at the PFA outlet is estimated as

$$C_k = C_{k,av} = \frac{\sum_1^M C_{k,m} V_m}{\sum_1^M V_m} \quad (12)$$

where $C_{k,m}$ is the concentration of the specie k at the output of the module m , M is the number of parallel modules in the PFA, and $V_m = U_m/\rho_m$ is the volumetric flow velocity at the outlet of the module m (ρ_m is the density of water at the outlet of the module m).

All components outside of the PFA are considered as a single block with an aqueous temperature of 70 °C and a residence time of 50 s during the irradiation (i.e., burn) period, which is part of one revolution of the entire cycle.

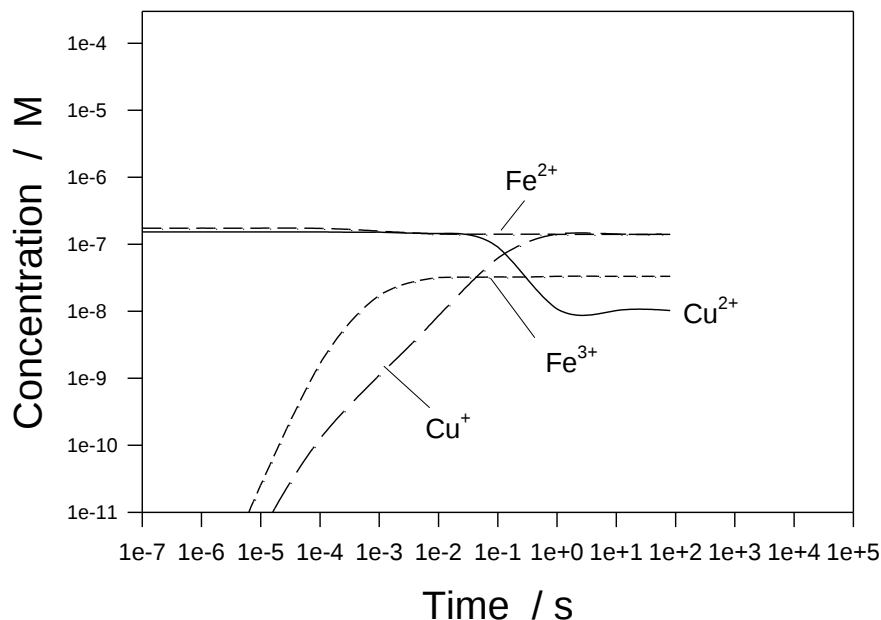


Figure 34. Predicted concentrations of metal species in an average equatorial module as a function of time. Initial conditions are $[Cu^{2+}] = 10$ ppb, $[Fe^{2+}] = 10$ ppb, and $[Cu^+] = [Fe^{3+}] = 0$. $[H_2]_{inlet} = 1$ cc(STP)/kg H_2O .

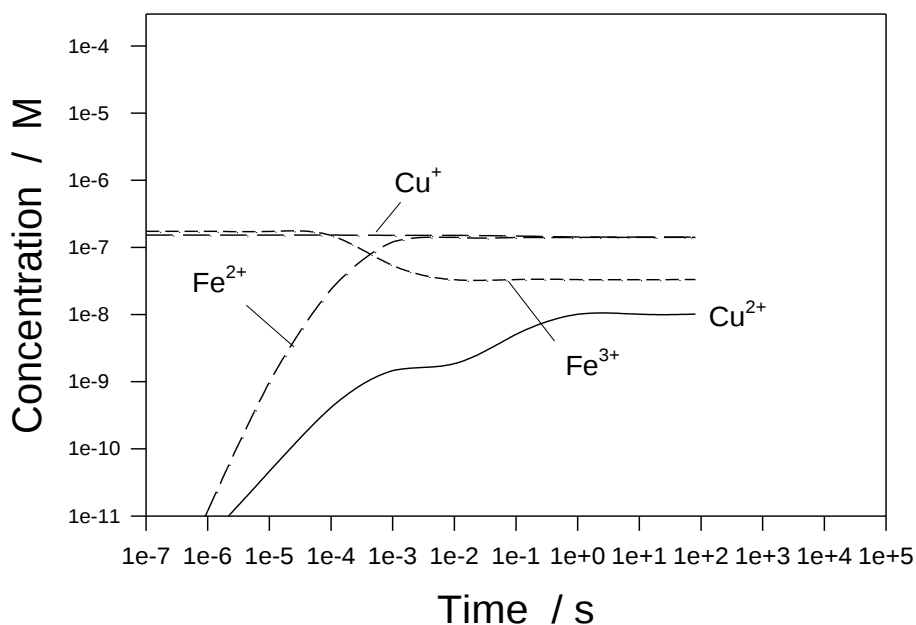


Figure 35. Predicted concentrations of metal species in an average equatorial module as a function of time. Initial conditions are $[Cu^+] = 10$ ppb, $[Fe^{3+}] = 10$ ppb, and $[Cu^{2+}] = [Fe^{2+}] = 0$. $[H_2]_{inlet} = 1$ cc(STP)/kg H_2O .

If the concentrations of the radiolysis species at the PFA inlet and the conditions within the PFA are known, the concentrations of radiolysis species at the outlet of each module can be calculated, as well as the average concentrations of radiolysis species at the PFA outlet via Equation (12). An example of these calculations with the addition of 1 cc (STP)/kg H_2O

of hydrogen is shown in Figures 36 and 37 (marked by revolution cycles 0 to 13) [1,35]. The concentrations marked by cycles = 0 in Figure 36 correspond to the initial conditions in the IBED PHTS. After that, the coolant, containing the species at the calculated concentrations, flows to the PFA outlet (marked by Cycle 1 in Figure 36), then passes through the OPFA, and concentrations of species at the PFA inlet (marked by Cycle 1 in Figure 36) are used as input data for the PFA to calculate the average concentrations at the Plasma Flux Area outlet for the next cycle (marked by Cycle 2 in Figure 37). This process, which is repeated thirteen times in our calculations, is representative of events within an envisioned plasma “burn” period in IBED PHTS operation.

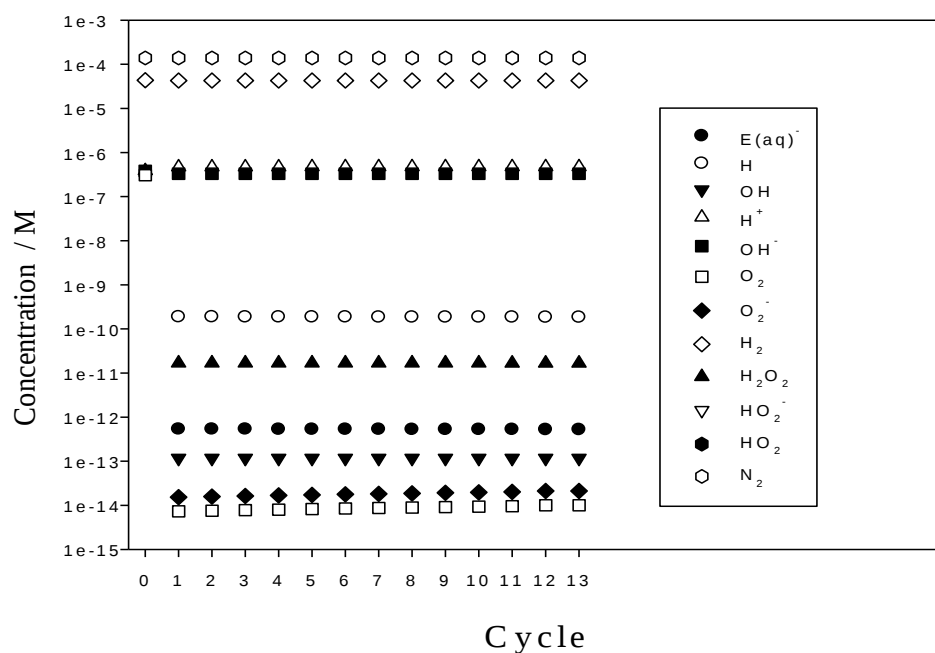


Figure 36. Calculated average concentrations of radiolysis species at the Plasma Flux Area inlet as a function of the number of revolution cycles. $[H_2]_{inlet} = 1 \text{ cc (STP)/kg } H_2O$.

As seen in Figures 36 and 37, stabilization of the concentrations of the radiolysis species already occurs after the first cycle. This means that there is no accumulation of radiolysis products in the OPFA in the IBED PHTS if a super stoichiometric amount of hydrogen (i.e., greater than that generated by radiolysis) is injected into the coolant water. Furthermore, during plasma the plasma burn period, as the coolant moves through the OPFA, almost complete decomposition of radiolysis products that were generated in the Plasma Flux Area occurs. An exception is hydrogen peroxide, which can have high production rates in some PFA modules and slowly accumulates in the system during plasma cycle. Although currently there is no hydrogen peroxide limit in the IBED PHTS, the corrosion impact of the hydrogen peroxide level should be carefully evaluated by estimating the ECP and crack growth rate for a standard crack in a structural alloy, for example, as is done in Part II [291]. Briefly, because an operating reactor will have a wide distribution in crack length, reflecting a wide distribution in crack initiation time and distributions in the stress intensity factor (stress), in the ECP, and in crack growth rate, it is necessary to define a “standard crack” to characterize the relative severities of the environment toward IGSCC. For the present purposes, the “standard crack” is defined as one having a crack length of 0.5 cm loaded to a stress intensity factor of $25.0 \text{ MPa} \cdot \text{m}^{1/2}$. The “standard crack” concept is addressed further in Part II of this series [291].

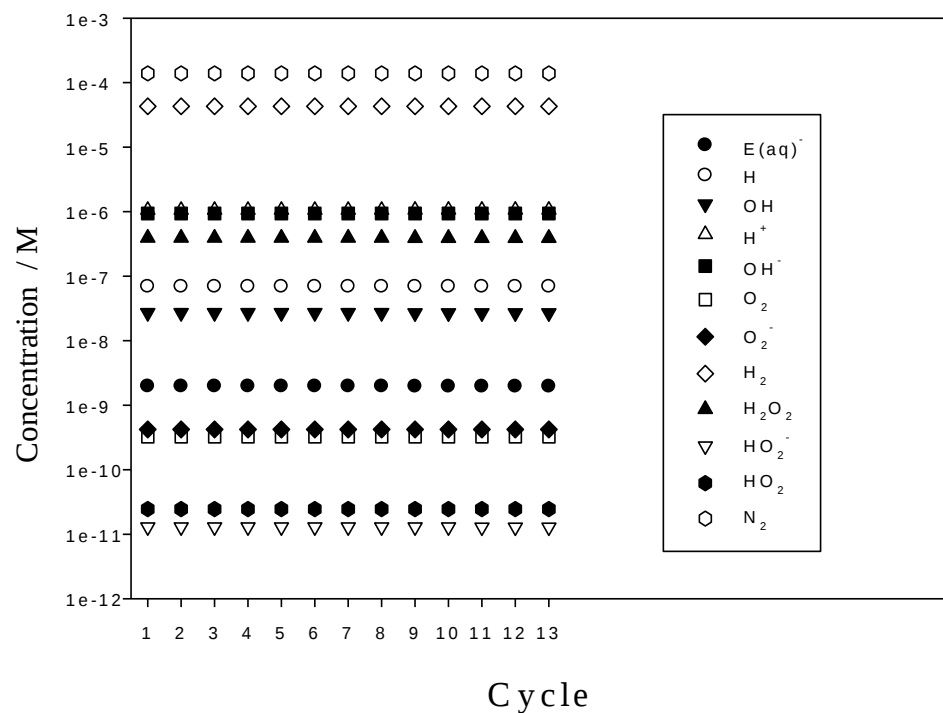


Figure 37. Calculated average concentrations of radiolysis species at the Plasma Flux Area outlet as a function of the number of revolution cycles. $[H_2]_{\text{Inlet}} = 1 \text{ cc (STP)/kg H}_2\text{O}$.

Because the resulting concentration of oxygen in IBED PHTS during the plasma burn with hydrogen addition is below the target level (10 ppb), there is no pressing need to remove oxygen from the coolant water. However, a degassing function of CVCS via fractional clean-up will be needed during all other modes of operation of the IBED PHTS. Moreover, the CVCS is needed to control concentrations of Cu, Fe, and other impurities in the system.

The concentrations of the three principal radiolysis products (H_2 , O_2 , and H_2O_2) at the PFA outlet and at the PFA inlet for the next coolant cycle (i.e., after passing for 50 s through the OPFA) are summarized in Tables 23 and 24, respectively. It must be noted that because the relaxation time (the time over which the species concentrations change during formation, Figure 32, or recombination) in the OPFA ($<1 \text{ s}$) is much less than residential time in this area (50 s), the concentrations at the PFA inlet can be considered as the concentrations inside the main part of OPFA of the previous cycle.

Table 23. Steady-state concentrations of H_2 , O_2 , and H_2O_2 as a function of the concentration of hydrogen added to the coolant for the simulated environment in an average Equatorial Port module located in the PFA of the IBED PHTS.

$[H_2]_{\text{Input}}$	$[H_2]_{\text{Input}}$	$[H_2]_{\text{Input}}$	$[H_2]_{\text{ss}}$	$[O_2]_{\text{ss}}$	$[H_2O_2]_{\text{ss}}$	$[H_2]_{\text{ss}}$	$[O_2]_{\text{ss}}$	$[H_2O_2]_{\text{ss}}$
cc (STP)/kg H_2O	M	ppb	M	M	M	ppb	ppb	ppb
0	0	0	1.53×10^{-5}	4.37×10^{-6}	6.02×10^{-6}	31.7524	144.8283	212.1415
0.1	4.31×10^{-6}	8.9229	1.05×10^{-5}	4.80×10^{-7}	6.03×10^{-6}	21.6517	15.9027	212.4514
0.2	8.61×10^{-6}	17.8442	1.28×10^{-5}	1.26×10^{-7}	4.84×10^{-6}	26.5881	4.1772	170.4914
0.5	2.15×10^{-5}	44.6146	2.32×10^{-5}	1.60×10^{-8}	2.48×10^{-6}	48.101	0.5303	87.2583
1	4.31×10^{-5}	89.2292	4.37×10^{-5}	2.79×10^{-9}	1.38×10^{-6}	90.4824	0.0925	48.5876
10	4.37×10^{-4}	892.2089	4.31×10^{-4}	1.92×10^{-11}	5.95×10^{-7}	891.8567	6.38×10^{-4}	20.9557

Table 24. Steady-state concentrations of H_2 , O_2 , and H_2O_2 as a function of the concentration of hydrogen added to the coolant for the simulated environment at the PFA inlet of the IBED PHTS after 50 s transit through the OPFA from the PFA outlet of the previous cycle. These concentrations can be also considered as the concentrations within the OPFA.

$[H_2]_{\text{Input}}$ cc (STP)/kg H_2O	$[H_2]_{\text{Input}}$ M	$[H_2]_{\text{Input}}$ ppb	$[H_2]_{\text{ss}}$ M	$[O_2]_{\text{ss}}$ M	$[H_2O_2]_{\text{ss}}$ M	$[H_2]_{\text{ss}}$ ppb	$[O_2]_{\text{ss}}$ ppb	$[H_2O_2]_{\text{ss}}$ ppb
0	0	0	3.70×10^{-6}	2.13×10^{-6}	1.83×10^{-10}	7.5569	70.5978	6.44×10^{-3}
0.1	4.31×10^{-6}	8.9229	3.74×10^{-6}	3.53×10^{-14}	1.66×10^{-11}	7.6366	1.17×10^{-6}	5.85×10^{-4}
0.2	8.61×10^{-6}	17.8442	8.43×10^{-6}	1.33×10^{-14}	1.69×10^{-11}	17.2391	4.41×10^{-7}	5.95×10^{-4}
0.5	2.15×10^{-5}	44.6146	2.09×10^{-5}	8.18×10^{-15}	1.69×10^{-11}	42.7094	2.71×10^{-7}	5.95×10^{-4}
1	4.31×10^{-5}	89.2292	4.24×10^{-5}	7.10×10^{-15}	1.68×10^{-11}	86.7085	2.35×10^{-7}	5.92×10^{-4}
10	4.37×10^{-4}	892.2089	4.30×10^{-4}	6.47×10^{-15}	1.68×10^{-11}	879.0623	2.14×10^{-7}	5.92×10^{-4}

Analysis of Tables 23 and 24 shows that the concentration of oxygen in the model block in Plasma Flux Area (Table 21) is sensitive to the concentration of input hydrogen with $[O_2]$ decreasing from 144.8 ppb to 6.38×10^{-4} ppb upon the addition of 10 cc (STP)/kg H_2O (0.9 ppm) of hydrogen to the circuit; a reduction by a factor of 2×10^5 . On the other hand, $[H_2O_2]$ is predicted to decrease from 212.1 to 21.0 ppb, a factor of 10.1. Thus, hydrogen added to the circuit from an external source (e.g., in the CVCS) is much more effective in suppressing the formation of oxygen in the PFA than it is in suppressing the formation of hydrogen peroxide—a fact that was known from previous fission reactor (BWR) studies [216] and from previous modeling of the ITER (e.g., [27,28]). In the absence of added hydrogen, the $[O_2]$ decays from 144.82 ppb at the model block in PFA outlet to 70.6 ppb at the PFA inlet on the following cycle: a decrease by a factor of 2.05. This occurs via the radiolysis model (e.g., Table 5) acting in reverse, due to the loss of the radiolysis source terms (Q_n and Q_γ) in Equation (9): these terms in the OFA are equal to zero. Under the same conditions, the concentration of H_2O_2 decays from 212.1 ppb to 6.44×10^{-3} ppb; a factor of 3.3×10^3 . With the addition of 10 cc (STP)/kg H_2O (0.9 ppm), the $[O_2]$ decreases from 6.38×10^{-4} ppb to 2.14×10^{-7} ppb, or by a factor of 2.9×10^3 , while $[H_2O_2]$ decays from 20.1 ppb to 5.91×10^{-4} ppb, or by a factor of 3.5×10^4 . Thus, hydrogen has only a modest impact on the decay of H_2O_2 but greatly enhances the decay of O_2 in the OPFA. This is because the primary mode of decay of H_2O_2 in the absence of irradiation is due to Reaction 30, Table 5, $2H_2O_2 \rightarrow 2H_2O + O_2$. On the other hand, the primary mode of decay of O_2 is the reaction with hydrogen via the reverse of the radiolysis mechanism.

In the OPFA (Table 23), with the addition of a super stoichiometric concentration of hydrogen ($[H_2]_{\text{Inlet}} > 0$), the concentrations of O_2 and H_2O_2 are reduced to a very low level but, nevertheless, are considerably greater than the thermodynamic equilibrium values, due to residual amounts that are not completely annihilated by recombination with hydrogen via the reverse of the radiolysis mechanism (O_2) and thermal decomposition (H_2O_2). These residual amounts of these oxidizing agents displace the ECP slightly in the positive direction from the value in their absence, as is discussed in Part II [291].

Apparently, the focus on “suppression of radiolysis” by monitoring dissolved oxygen is somewhat misplaced from a corrosion viewpoint because H_2O_2 is the more powerful oxidizing agent, on a molar basis, than is O_2 , and it is much more potent than is oxygen in raising the ECP and in increasing the driving force for general corrosion and the various forms of localized corrosion (e.g., IGSCC in sensitized austenitic stainless steels).

5. Summary and Conclusions

An analysis has been performed on various models proposed to describe the radiolysis of water in the PHTSs of fission and fusion (i.e., ITER) reactors, with the objective of assessing their physico-chemical viabilities and for predicting the generation of various, deleterious radiolysis products in reactor coolant circuits with emphasis on the ITER. Although further analysis is required, several important issues have been identified.

- The models appear to be massively underdetermined; the number of unknown model parameters far exceeds the number of independent experimental observations. This issue has been partly overcome by assuming that the reactions between highly energetic radiolysis species (e.g., H, OH, e_{aq}^-) are diffusion controlled and hence the rate constants and activation energy can be calculated from kinetic diffusion theory. Nevertheless, the problem remains.
- In some cases, not all reactions in the model are “elementary” in that they have reaction orders greater than two. In these cases, non-elementary reactions can be broken down to yield two or more elementary reactions, some of which are already contained in the models.
- All models assessed to date contain reactions between species of like charge (e.g., $e_{aq}^- + e_{aq}^- \rightarrow 2OH^- + H_2$), which are judged to be improbable under near-ambient conditions upon the grounds of coulombic repulsion. After all, the reaction between D (2H_1) and T (3H_1) requires a temperature of about 20 keV (equivalent to about 300,000,000 K) to cause fusion of the nuclei, while under near-ambient conditions the available energy is on the order of 25 to 40 meV. Thus, reactions between species of like charge can be discarded as being impossible under the conditions of the ITER coolant. The fundamental problem with this reaction is that it may be decomposed into three elementary reactions that already exist in the models as follows: $[2(e^- + H_2O \rightarrow OH^-) + H + H \rightarrow H_2]$, each of which does not involve reaction between species of like charge. Thus, the offending reaction, $e_{aq}^- + e_{aq}^- \rightarrow 2OH^- + H_2$, can be discarded. Reactions of this type that appear in various “mechanisms” proposed for the radiolysis of water are summarized in Table 5 together with the chemical kinetic conditions that they violate. If these elementary reactions are present in a model, the parent reaction is assigned a rate constant of zero, thereby effectively removing it from the model.
- Few of the proposed models yield the overall stoichiometric reaction or satisfy charge and mass balance constraints. This basic requirement of any physico-chemical model must be demonstrated unequivocally before a model is accepted.
- Previous work has shown that the uncertainty in the radiolytic yields (i.e., G-values) can have a significant impact on the calculated radiolytic species concentrations and upon the calculated corrosion potential and crack growth rate. In particular, it is recommended that an assessment be made to identify the “best available” set of primary G-values that also recognizes the importance of LET in the radiolysis of water by highly energetic neutrons.
- Hydrogen must be added to the circuit from an external source to suppress radiolysis under ITER IBED PHTS operating conditions. In the absence of added hydrogen, the concentration of oxygen is predicted to increase above the allowed level (i.e., 10 ppb) by at least one order of magnitude. However, injection of a small amount of hydrogen (i.e., approximately 1 cc (STP)/kg H_2O or 0.09 ppm) is predicted to decrease the concentration of oxygen in the system by two orders of magnitude below the allowed level, as well as to substantially reduce the concentration of hydrogen peroxide by about a factor of 0.23. The addition of hydrogen has much more pronounced effect in suppressing the formation of oxygen in the Plasma Flux Area than it does in suppressing the formation of hydrogen peroxide. These findings agree with those resulting from modeling fission reactors (i.e., BWRs and PWRs).
- The cations of Cu and Fe are predicted to be in their lower valence form in the IBED PHTS. If the concentrations of these ions do not increase above 10 ppb, these ions will have no significant influence on the radiolysis of water in the IBED PHTS. However, the presence of Cu and Fe in the solution might affect the rates of heterogeneous reactions that influence corrosion processes.
- Calculations predict that there is no accumulation of radiolysis products in the Plasma Flux Area (PFA) under the operating conditions during the burn and dwell periods. The model predicts that there are practically no radiolysis products at the inlet of

the PFA after the coolant has passed through the OPFA, and the concentrations of all species in the OPFA do not change with time if a certain level of hydrogen is ejected into the water. This means that there is no need to remove oxygen from water during plasma burn because the concentration of oxygen is below the allowed level (10 ppb) and the hydrogen concentration does not change in any module of the IBED PHTS. However, degassing function of CVCS via fractional clean-up will be needed during all other modes of operation of the IBED PHTS. Moreover, the CVCS is needed to control concentrations of Cu, Fe, and other impurities in the system.

- The concentrations of all species practically do not change in the main part of each module in the IBED PHTS. These concentrations are approximately equal to their steady-state concentrations under the fluid conditions in the corresponding module. In this relation, the corrosion condition inside each module can be characterized by the single value of ECP.
- The focus on “suppression of radiolysis” by monitoring dissolved oxygen is apparently misplaced because H_2O_2 is the more powerful oxidizing agent, on a molar basis, than is O_2 , and it is much more potent than is oxygen in raising the ECP and in increasing the driving force for general and the various forms of localized corrosion.

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