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Environmental controls for higher temperature direct-cycle light water reactors

John A. Wilson [a,*], Raj Pathania [b], Samson Hettiarachchi [c]

[a] Exelon Corporation, 4300 Winfield Road, Warrenville, IL 60555, United States
[b] Electric Power Research Institute, 3420 Hillview Avenue, Palo Alto, CA 94304, United States
[c] GE-Hitachi Nuclear Energy, 6705 Vallecitos Road, Sunol, CA 94586, United States

ABSTRACT

Radiolysis modeling is used to estimate the minimum hydrogen concentration to activate platinum catalysts and reduce the electrochemical corrosion potential in light water reactors. Platinum catalysts are used in boiling water reactors to catalyze hydrogen and oxygen recombination, which reduces the corrosion potential and the susceptibility of austenitic structural materials to intergranular stress corrosion cracking. Two environmental challenges for material performance in higher temperature light water reactors are the increased susceptibility of austenitic materials to stress corrosion cracking and the higher production rate of oxidizing radiolytic species. For a reference supercritical water reactor, a hydrogen addition rate of 2 standard cubic feet per minute is needed to significantly reduce the susceptibility of austenitic materials to stress corrosion cracking. Also, for a reference higher temperature boiling water reactor, a hydrogen addition rate of 10 standard cubic feet per minute of hydrogen reduces the stress corrosion crack susceptibility of austenitic materials located in the lower portion of the reactor vessel.

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1. Introduction

Structural materials used in the current generation of the light water reactor (LWR) are being evaluated for use in the supercritical water reactor (SCWR) [1]. Austenitic stainless steels and nickel alloys used in the current generation of LWR are more susceptible to intergranular stress corrosion cracking (IGSCC) at higher temperatures and in the oxygenated environment of a direct-cycle LWR. The susceptibility of these materials to IGSCC can be reduced by improved environmental controls. This paper proposes the use of heterogeneous catalysts, currently used in the boiling water reactor (BWR), for catalytic recombination of hydrogen and oxygen and suppression of the electrochemical corrosion potential (ECP) in the higher temperature direct-cycle LWR. The IGSCC susceptibility of these materials using catalytic suppression is discussed for two reactor concepts: a SCWR and a higher temperature BWR (HTBWR).

2. BWR environmental controls

BWRs were originally designed to operate with oxygenated reactor coolant. The source of reactor coolant oxygen is radiolysis of water in the core. Utilities experienced high maintenance costs due to IGSCC of austenitic stainless steel and nickel alloys caused by oxygen and high ECP in the reactor coolant. However, the pressurized water reactor (PWR) did not experience the early failure of these materials because hydrogen is maintained at 2.3–4.5 ppm (mass basis) in the primary coolant of the PWR to fully suppress oxygen production from radiolysis.

It is not economical to continually replace the hydrogen lost in the BWR off gas system and to maintain the 2.3–4.5 ppm hydrogen that is required for full radiolysis suppression. So, to mitigate the deleterious effects of oxygen, all BWRs in the US add lower levels of hydrogen that partially suppress radiolysis. When ECP is lowered below −230 mV Standard hydrogen electrode (SHE), by hydrogen addition, the susceptibility to SCC is dramatically reduced. In the 1980s and 90s, some BWRs operated with low levels of hydrogen, about 0.4 to ⩽1 ppm in the feedwater system (0.1–0.2 ppm in reactor coolant), to partially suppress radiolysis. This partial radiolysis suppression in BWRs reduced the ECP and mitigated SCC in the recirculation piping. In the early 90s, it was determined that feedwater hydrogen concentrations of 1–2 ppm were required to lower the ECP to mitigate IGSCC of reactor internals. The feedwater hydrogen concentration to lower the ECP for the piping and vessel internals is shown in Fig. 1. The impact with moderate hydrogen addition (1–2 ppm) is that the main steam radiation level increases by a factor of 3–5 due to N-16 carryover to steam phase. To minimize the increased main steam radiation levels, Hettiarachchi [2] developed catalytic ECP suppression for IGSCC mitigation.

For catalytic suppression of ECP, the reactor internal surfaces are made catalytic by deposition of micro gram per cm^2 levels of platinum and rhodium on the wetted surfaces. The ECP of catalytic surfaces in the reactor internals is lowered to <−500 mV (SHE)

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[*] Corresponding author. Tel.: +1 630 657 3807; fax: +1 630 657 4328.
E-mail address: johna.wilson@exeloncorp.com (J.A. Wilson).

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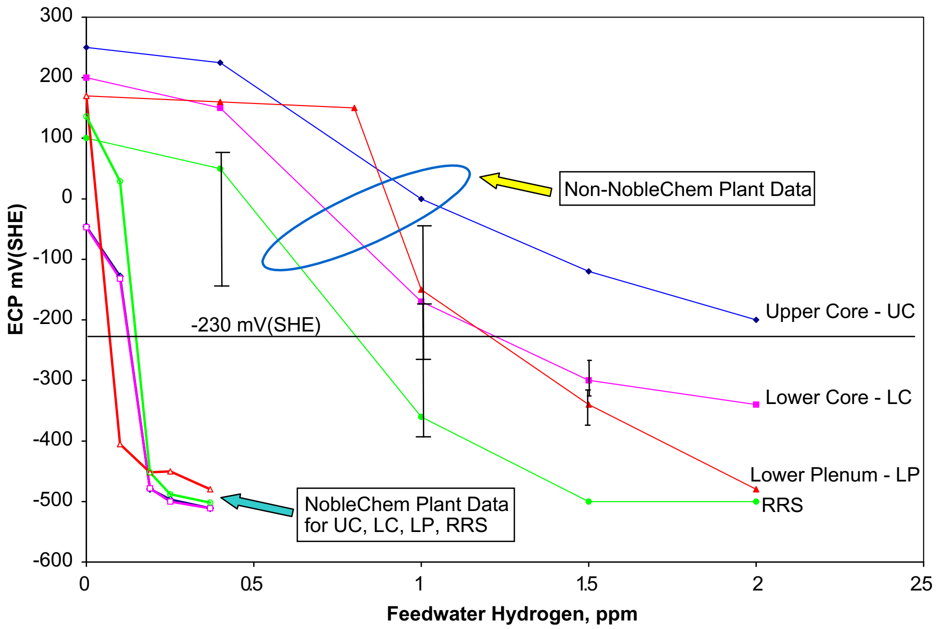

Fig. 1. Post-NobleChem™ and non-NobleChem™ BWR plant ECP data versus feedwater hydrogen concentration for different in-vessel locations.

with 0.1–0.2 ppm feedwater hydrogen (0.03–0.05 ppm in reactor water). The low ECP achieved in a BWR with catalytic suppression is similar to the low ECP in a PWR operating with high hydrogen. So, catalytic suppression in a BWR significantly reduces IGSCC susceptibility, similar to the full radiolysis suppression in a PWR. The deposition of platinum and rhodium metal in BWRs was demonstrated at the Duane Arnold BWR in 1996 and more than three-fourths of US BWRs are now using these catalysts. The most common application process occurs during a reactor outage. Chemicals containing noble metals are injected for approximately two days. This application is repeated typically every 6 years. In 2005 an on line noble metal process was successfully demonstrated at a BWR and has been applied at four plants. The catalytic suppression technology developed by General Electric-Hitachi (GEH) is called NobleChem™.

Fig. 1 [3] shows the ECP response of stainless steel to hydrogen addition in the feedwater. For a catalytic surface the ECP drops below −500 mV (SHE) when the hydrogen to oxygen molar ratio exceeds 2. For additional margin the feedwater hydrogen addition rate is adjusted to maintain a molar ratio of 3 for the internal components that are protected by catalytic suppression. Hydrogen and oxygen concentrations and ECP are measured in the recirculation piping system. To calculate the ECP for locations in the reactor vessel where ECP cannot be measured, GEH and EPRI developed the BWRVIA [4] radiolysis model. The BWRVIA model calculates the concentration of radiolysis products and the ECP for all piping and vessel internal locations. The radiolysis model uses thirty-six reactions including neutron and gamma *G*-values (number of molecules produced per absorbed energy of 100 eV). Ten of the reaction rates are adjusted to maximize agreement between model results and plant measurements of oxygen and hydrogen.

3. BWR/6 radiolysis model

The operating US BWRs include 5 GEH generations, BWR/2 thru BWR/6. Each BWR design requires its own BWRVIA model because of differences in neutron and gamma fluence, and in-vessel geometry and hydraulics. Fig. 2 shows the BWRVIA model output for one of the Exelon BWRs, Clinton Power Station, which is a BWR/6. Fig. 2 shows the reactor water hydrogen to oxygen molar ratio for selected piping and reactor vessel locations versus feedwater hydrogen. The vessel internal locations shown are the upper downcomer (DC-UP), the lower downcomer (DC-LO), the recirculation piping (RC_END), the bottom of the lower plenum (LP_BOT), and the top of the lower plenum (LP_UP). A molar ratio of 2 and ECP suppression is achieved for Clinton Power Station with 0.1 ppm feedwater hydrogen, but a feedwater hydrogen concentration of 0.2 ppm is maintained for operating margin.

Fig. 3 shows the BWRVIA model results for the reactor water hydrogen, oxygen, and total oxidant concentration at the upper downcomer location versus the feedwater hydrogen concentration for Clinton Power Station. The total oxidant is the sum of the two major oxidants produced by radiolysis, oxygen and hydrogen peroxide. The hydrogen peroxide is not soluble in steam and is carried over with the recycled coolant from the moisture separator into the upper downcomer region of the vessel. This causes the recycled coolant to be highly oxidizing because most of the hydrogen produced by radiolysis in the core is stripped into the steam phase and leaves the reactor vessel in the main steam. The feedwater enters the vessel in the upper downcomer region and mixes with the recycled coolant. Sufficient hydrogen is added into the feedwater to compensate for the hydrogen removed by the main steam, so that the molar ratio in the upper downcomer is >2. Fig. 3 shows that for catalytic suppression in the BWR/6 the minimum reactor coolant hydrogen concentration at the upper downcomer location required for catalytic ECP suppression is 0.03 ppm. For the reference BWR/6, 9 SCFM of hydrogen gas is injected into the feedwater to produce a 0.2 ppm feedwater hydrogen concentration. As shown in Fig. 3 and 0.2 ppm in the feedwater produces about 0.05 ppm hydrogen in the reactor coolant at the upper downcomer location.

4. Catalytic ECP suppression for higher temperature reactors

Table 1 compares characteristics of reference reactor designs to the SCWR [5] and the HTBWR. The two reference BWR designs shown in Table 1 are the BWR/6, which is the last constructed BWR in the US, and the ESBWR [6], which is the latest GE-Hitachi design. The ESBWR does not have recirculation loops and uses nat-

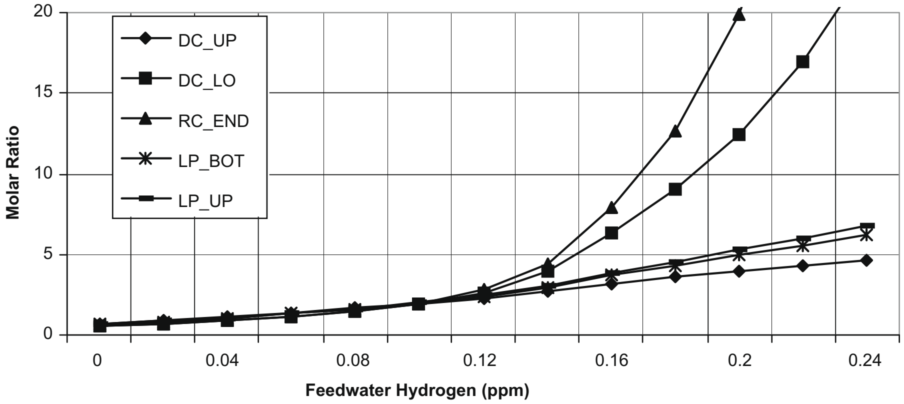

Fig. 2. BWRVIA model reactor water hydrogen to oxygen molar ratio predictions versus feedwater hydrogen concentration for different in-vessel locations for Clinton Power Station.

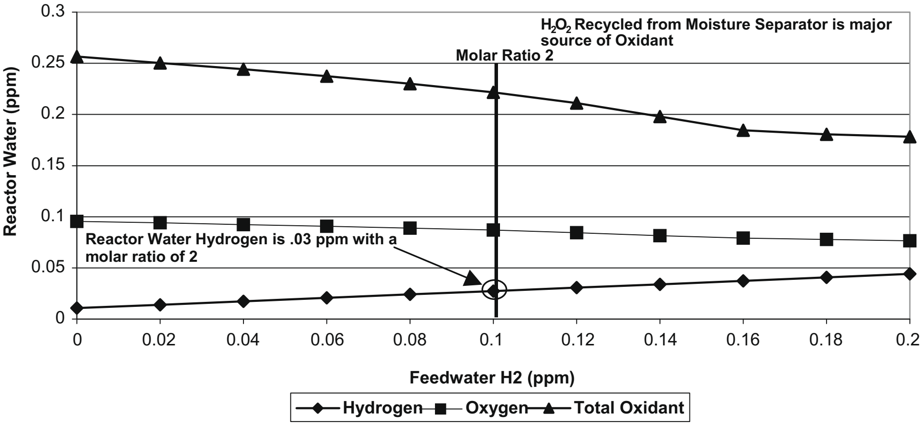

Fig. 3. BWRVIA model reactor water hydrogen, oxygen, and total oxidant concentration predictions versus feedwater hydrogen concentration for Clinton Power Station.

Table 1
Comparative characteristics of the reactors described in text.

Reactor type	BWR/6	ESBWR	HTBWR	SCWR	PWR
MWt	3579	4500	4500	3575	N/A
Inlet temp. (°C)	278	271	278	280	290
Outlet temp. (°C)	288	288	327	400	323
Recycle ratio	6	3.7–4.4	<3.7	Once thru	Once thru
Radiolysis suppression	Catalytic	Catalytic	Catalytic	Catalytic	Full
Reactor water H_2 (ppm)	0.05	0.05	0.05	0.05	2.2–4.5
SCFM H_2	9	~12	~12	<2	<0.1

ural circulation to drive the core flow. Compared to previous BWR designs, the ESBWR has a lower core inlet temperature of 271 °C because the reactor vessel recycle ratio has been reduced from 6 down to about 4. The recycle ratio is the core flow rate divided by the steam flow rate. The BWR/6 is operated with core inlet and exit temperatures of 274 and 288 °C, respectively. A typical PWR, shown in Table 1, has nominal cold leg, hot leg, and pressurizer temperatures of 290, 323, and 345 °C, respectively.

The HTBWR concept is a natural recirculation BWR, like the ESBWR, with core outlet temperatures 39 °C higher than the ESBWR. The core outlet temperature of the HTBWR, 327 °C, is bounded by the PWR operating experience. This provides confidence that the materials can perform reliably in the HTBWR for 60 years of plant operation. The core outlet temperature of the reference SCWR is 500 °C. However, a core outlet temperature of 400 °C is used for this evaluation because the austenitic materials evaluated may not operate for 60 years at 500 °C without IGSCC failures.

Table 1 also compares the hydrogen injection rates and the reactor water hydrogen concentration required for ECP suppression for each reactor. For PWRs the hydrogen addition rate is very low because very little hydrogen is lost in the closed primary coolant cycle. Typically, <0.1 SCFM hydrogen is required to make up for the hydrogen lost during fission gas removal.

Catalytic suppression reduces the ECP for all locations in the SCWR, including the core outlet. This is in contrast to the BWRs, which have high ECP and IGSCC susceptibility at the core outlet due to hydrogen stripping into the steam phase. The concentration of hydrogen required to achieve catalytic suppression with the SCWR can be calculated without a radiolysis model because there are no oxidants from recycle in the 'once thru' SCWR. Hydrogen and oxidants are produced stoichiometricly by radiolysis with a

Table 2
Electrochemical corrosion potential and 304 SS crack growth rates for the ESBWR, HTBWR, and SCWR at the core inlet, bypass and outlet locations.

Location	Core inlet		Core bypass		Core outlet	
Reactor	ECP mV(SHE)	CGR (mm/s)	ECP mV(SHE)	CGR (mm/s)	ECP mV(SHE)	CGR (mm/s)
ESBWR	−500	7.4×10^{-10}	−500	5.1×10^{-10}	+200	6.4×10^{-9}
HTBWR	−500	6.3×10^{-10}	−500	[a]	+200	[a]
SCWR	−500	6.1×10^{-10}	−500	[b]	−500	1.1×10^{-8}

[a] No laboratory crack growth rate data is available at the HTBWR core bypass and outlet temperatures.
[b] The SCWR has no core bypass flow.

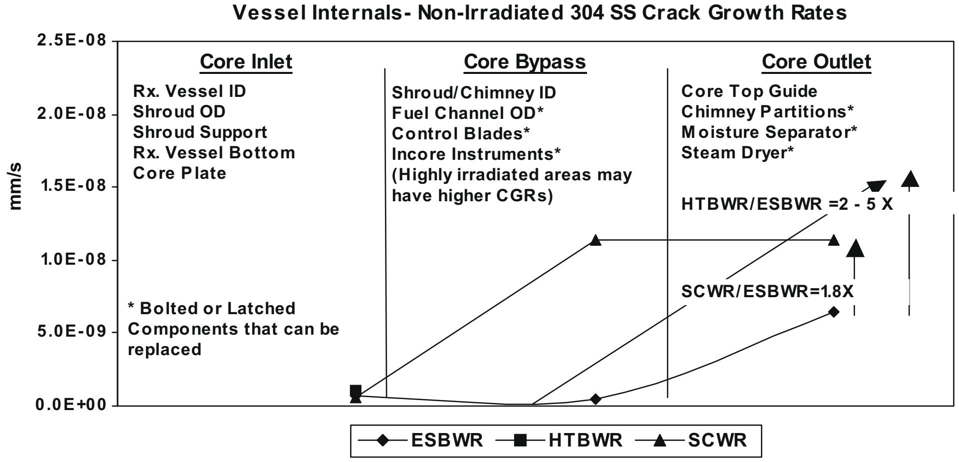

Fig. 4. Schematics of calculated 304 SS crack growth rates for the ESBWR, HTBWR, and SCWR for non-irradiated 304 stainless steel in reactor vessel internals with catalytic suppression.

molar ratio of 2. So, the only source of ‘extra’ oxygen in the SCWR is up to 0.2 ppm dissolved oxygen in the feedwater from air leaking into the main condenser. The molar ratio in the feedwater can be increased to 4 by adding hydrogen to maintain a concentration of 0.05 ppm. For the SCWR with a feedwater flow rate of 1843 kg/s, this corresponds to a hydrogen injection rate up to 2 SCFM. However, the solubility of some chemical species in supercritical water is not known, which increases the uncertainty of extrapolating the experience from sub-critical water reactors to the SCWR.

The BWRVIA model will need to be extended to the ESBWR and HTBWR to accurately calculate the required hydrogen injection rate for catalytic suppression. However, hydrogen injection rates can be estimated based upon the hydrogen required for the BWR/6. The reactor water hydrogen concentration for catalytic suppression in the BWR/6 is 0.05 ppm. So, the hydrogen injection rate required for catalytic suppression for the ESBWR and HTBWR is estimated by calculating the hydrogen injection rate required to achieve the reactor water hydrogen concentration of 0.05 ppm. The hydrogen injection rate for the ESBWR will be higher than for the BWR/6 because of the higher power rating and feedwater flow rate. Based upon the ratio of the feedwater flow rates, the ESBWR hydrogen injection rate for catalytic suppression is estimated to be about 12 SCFM.

For the HTBWR, the *G*-values for radiolysis [7] are higher than for the ESBWR due to the higher HTBWR temperature. The higher *G*-values increase the oxidant concentration in the reactor coolant, which increases the requirement for hydrogen addition for the HTBWR. However, the decomposition rate of hydrogen peroxide is also higher at the higher temperatures with an activation energy of 48 kcal/mole [8]. The hydrogen peroxide that decomposes into oxygen at the core exit will partition into the steam and not be recycled by the moisture separator. So, the more rapid decomposition of hydrogen peroxide in the HTBWR decreases the hydrogen demand. With the offsetting effects of higher *G*-values and higher hydrogen peroxide decomposition rates for the HTBWR, hydrogen demand for the HTBWR is expected to be 12 SCFM, which is similar to the ESBWR. A revision of the BWRVIA model that incorporates the temperature dependence of the rate constants will be required to accurately determine the required hydrogen addition rate for catalytic suppression in the HTBWR.

5. SCC susceptibility

The temperatures and ECPs described in the previous section are the two most significant environmental conditions that affect the susceptibility of austenitic stainless steel and nickel alloys to SCC. This paper uses the 304 SS ECP and crack growth correlations in the literature to evaluate the effectiveness of catalytic suppression to reduce SCC susceptibility. The ECPs used for the crack growth rate calculations are +200 mV(SHE) for an oxidizing environment and −500 mV(SHE) for catalytic suppression. The temperature range of crack growth rate data in the literature is applicable to the temperature of the core inlet and outlet temperatures for the ESBWR and the SCWR. However, additional data is required at 327 °C for the HTBWR core outlet. The HTBWR crack growth rates are expected to be similar to the ESBWR because measured activation energies in the region of 288 °C have varied from positive to negative. The calculated best-fit crack growth rate [9] for the ESBWR core outlet at + 200 mV(SHE) is 6.4×10^{-9} mm/s and the core inlet at −500 mV(SHE) is 7.4×10^{-10} mm/s. These rates were calculated for a stress intensity of 25 MPa$\sqrt{m}$ and a conductivity of 0.1 μS/cm. The SCWR core inlet crack growth rate under catalytic conditions (−500 mV), calculated using the same method as described for the HTBWR, is 6.1×10^{-10} mm/s. The crack growth rate at the high temperature of the SCWR outlet is expected to be significantly higher. Crack growth rates of stainless steel under these conditions have been measured at 1.1×10^{-8} mm/s [10]. The calculated crack growth rates for the ESBWR, HTBWR, and the SCWR are shown in Table 2 for three locations, the core inlet, the core bypass, and the core outlet.

6. Conclusions

Catalytic suppression reduces the ECP for all vessel internal locations for the SCWR and for the core inlet and core bypass regions of the HTBWR. Measured and calculated crack growth rates for the ESBWR, HTBWR, and SCWR are shown schematically in Fig. 4. The internal components located in the core inlet region (most expensive to replace) of both the SCWR and the HTBWR remain catalytic with crack growth rates $\leqslant 1 \times 10^{-9}$ mm/s, similar to the ESBWR. The internal components of the SCWR that are located in the core outlet region have a factor of 1.8 higher crack growth rate compared to the ESBWR core outlet because of the higher SCWR operating temperature. The core outlet crack growth rate may also be higher for the HTBWR, but cannot be calculated because there are no representative measurements at the relevant temperature. Estimates using reasonable activation energies indicate that the HTBWR core outlet crack growth rates could be factors of 2–5 higher, compared to the ESBWR. IGSCC degradation of reactor internals for the HTBWR and the SCWR can be reliably and economically managed because IGSCC susceptibility is suppressed in the lower vessel internals and is significantly reduced in the upper vessel internals. Most of the components at the core exit are bolted or latched, so if inspections indicate that components could fail before the end of their planned life, then these components could be replaced during a maintenance outage.

Additional experimental work should measure the stainless steel and nickel alloy crack growth rates at the HTBWR and SCWR core outlet temperatures. Also, the BWRVIA radiolysis model should be revised to include the higher temperature *G*-values and rate constants for the HTBWR and SCWR.

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