

STUDY OF CORROSION PRODUCT ACTIVITY DUE TO NON-LINEARLY RISING CORROSION RATES COUPLED WITH PH EFFECTS FOR LONG-TERM OPERATING CYCLES IN PRESSURIZED WATER REACTORS

by

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Scientific paper

DOI: 10.2298/NTRP1202178M

This work is a study of changes in coolant activity due to corrosion products of extended burn-up cycles of 18-24 months duration, in a typical pressurized water reactor, under pH and boric acid variations. It deals with non-linearly changing corrosion rates coupled with pH effects. The CPAIR-P computer program was modified to accommodate for time-dependent rising corrosion and effects of coolant chemistry. These simulations suggest that the effect of an increase in pH value for an extended 24-month cycle on a specific activity, in the form of a decrease in the said activity, is smeared by the rising corrosion. The new saturation values for activity at the end-of-cycle are lower than with a reactor operated at constant low pH/natural boric acid in the coolant. For a non-linear rise in the corrosion rate coupled with a pH rise from 6.9 to 7.4 and the use of enriched boric acid (30%-40%), coolant activity first rises to a peak value during the cycle and then approaches a much smaller saturation value at the end of the cycle, when compared with the activity for the system having a constant low pH value (6.9) in the coolant. In this work, we have shown that the use of enriched boric acid as a chemical shim actually lowers primary coolant activity when higher pH values, rather than natural boric acid, are employed in the coolant. For multiple long-term operating cycles, the saturation value of corrosion product activity increases in the first two cycles and becomes constant in subsequent ones, due to the high operational pH value for enriched boric acid (40%) as a chemical shim.

Key words: computer modeling and simulation, corrosion products, pH value, enriched boric acid, pressurized water reactor, extended operating cycle

INTRODUCTION

Several studies on pressurized water reactors (PWR) have shown that enriched boric acid (EBA) reduces the needed concentration and elevated value of pH (~7.4) can be achieved by using an acceptable 2.2 ppm of lithium without corrosion cracking problems [1-4]. Then the discharged burn-ups can be substantially increased to 40-50 MWd/kgU, as compared to previous generations having an average burn-up of 33 MWd/kgU. Such long-term operating cycles are based on higher initial enrichments and/or higher fuel loading and better neutron absorption at the beginning of the cycles.

Moreover, it was also perceived that corrosion products were mostly composed of magnetite (Fe_3O_4) in the primary loop. However, recent studies have shown that corrosion products are mainly composed of nickel-ferrite ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$) [5]. Therefore, for such systems, higher pH levels of 7.4 are more suited, as compared to the pH value of 6.9 for the primary coolant. It has also been observed that corrosion product activity can be minimized by using high pH values. The primary coolant in PWR becomes very corrosive due to high prevalent values of temperature and pressure in the system and the decomposition of water by radiation further increases its corrosive nature. Corrosion products may originate as soluble and insoluble oxides or in a number of other forms. The rate of corrosion in the reactor's primary system keeps increasing as the time of its operation at full power increases [6,

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7]. However, high pH values can minimize the corrosion rate and corrosion product activity in the primary circuit.

In the reactor core, corrosion products become activated due to neutron irradiation and their subsequent buildup in the core, the primary coolant and on piping inner surfaces taking place due to their lifelong exposure. Large end-of-cycle radioactivity can prohibit prompt access to the primary pumps, valves and their vicinity. The build-up of activity in the circulating coolant, inner surfaces of the coolant piping and the core surfaces does, indeed, create problems regarding the operation and maintenance of the reactor in terms of accessibility demands [8-11].

Corrosion product activity in PWR is primarily due to the short-lived ^{56}Mn and ^{24}Na . Nearly all of the long-lived activity in the coolant is due to iron, molybdenum, and cobalt, the most significant radionuclides being ^{59}Fe , ^{99}Mo , and ^{60}Co . Various nuclear properties of these nuclides are summarized in tab. 1 [12]. ^{55}Mn has an activation cross section of 13.4 b for the thermal neutrons to produce ^{56}Mn . The neutron activation of structural ^{27}Al and the activation of ^{23}Na from salt impurities in water can produce ^{24}Na . The use of high-purity water, demineralization of water and the presence of filters keep the amount of dissolved salts to less than 0.05 ppm [9]. However, the half-lives of the dominant corrosion products are longer than two hours. Therefore, the primary coolant retains the activity for several hours, even after reactor shutdown, and any transient condition during operation can further increase the end-of-cycle coolant activity [10, 11].

Experimental data on Corrosion Product Activity (CPA) is generally inaccurate due to problems re-

lated to the withdrawing of representative samples from the PWR primary coolant through long sampling lines. The measured values of concentrations of some corrosion products, (*e. g.*, soluble ^{60}Co , ^{58}Co , and ^{54}Mn), are strongly dependent on the sampling flow rate, pH values and boron concentration [13, 14]. Operating parameters of the reactor also strongly affect the types of radionuclides formed, levels of saturation activity reached and the rates at which saturation is achieved. These parameter include the composition of materials in contact with the coolant, the amount and types of impurities present in the coolant, reactor power, residence time of the coolant in the core, temperatures, pressure, coolant flow rates, corrosion rates, filter efficiency and deposition rates of radioactive elements in the coolant.

Several studies on coolant activation in PWR and the effects of flow rate and power perturbations were carried out. Simulations of low and high-flux systems have shown that transients under reactivity and loss of flow lead to the peaking of the neutron flux in the reactor and the production of activity in the coolant [8, 15]. This strongly affects coolant activity and corrosion rates. The void coefficient, Doppler coefficient and the temperature of the moderator exhibited significant effects on power peaking in a non-uniform manner within the core.

Venz *et al.* have shown that, in extended operating cycles of PWR, the chemistry of the reactor coolant plays an important role and that the dose in the primary coolant circuit at the nuclear power plant Beznau was lowered when the pH level was increased to 7.4 [16]. Also, the evaluation of corrosion product activity in PWR as a function of variations in the primary coolant chemistry for a long-term operat-

Table 1. Various prominent activation products and their reaction properties*

Corrosion products	Reaction and neutron energy	Activation cross-section and half-life	γ -ray energy MeV (intensity %)
^{24}Na	$^{27}\text{Al}(n, \alpha)^{24}\text{Na}$ ($E_n > 11.6$ MeV)	$6 \cdot 10^{-32} \text{ m}^2$	1.368 (99.994)
	$^{23}\text{Na}(n, \gamma)^{24}\text{Na}$ (E_n is thermal)	$5.3989 \cdot 10^4 \text{ s}$ $0.53 \cdot 10^{-28} \text{ m}^2$ $5.3989 \cdot 10^4 \text{ s}$	2.754 (99.855)
^{56}Mn	$^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ (E_n is thermal)	$1.34 \cdot 10^{-27} \text{ m}^2$	0.8467 (98.85)
		$9.2808 \cdot 10^3 \text{ s}$	1.8107 (26.9) 2.1131 (14.2) 2.5231 (1.02)
^{59}Fe	$^{58}\text{Fe}(n, \gamma)^{59}\text{Fe}$ (E_n is thermal)	$0.9 \cdot 10^{-28} \text{ m}^2$	0.1426 (1.02)
		$(1.6018 \cdot 10^5 \text{ s})$	0.1923 (3.08) 1.0992 (56.5) 1.2916 (43.2)
^{60}Co	$^{59}\text{Co}(n, \gamma)^{60}\text{Co}$	$2 \cdot 10^{-27} \text{ m}^2$	1.1732 (99.85)
		$(1.6638 \cdot 10^8 \text{ s})$	1.3325 (99.98)
^{99}Mo	$^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$ $E_n > 3.1$ MeV	$0.45 \cdot 10^{-28} \text{ m}^2$	0.1811 (6.14)
		$(2.3751 \cdot 10^5 \text{ s})$	0.3664 (1.20) 0.7395 (12.26) 0.7779 (4.3)

* Interactive chart of radionuclides NuDat 2.6, NNDC databases, Brookhaven National Laboratory (<http://www.nndc.bnl.gov/nudat2/chartNuc.jsp>)

ing cycle was done by Song *et al.* [17]. The program involves the modeling of CRUD, a colloquial term for corrosion products and rust & wear particles which become radioactive as they pass through a prevalently neutron field inside the core of a nuclear reactor. The authors used the COTRAN code based on a two-layer model and predicted that every subsequent generation of CRUD will increase as the operation cycle duration increases. They also predicted that enriched boric acids in the coolant reduce the amount of CRUD and that high pH operation periods, thus, become possible.

For acid-free coolants, the modeling of time-dependent CPA due to corrosion products in the primary coolants of PWR under various perturbations were carried out in order to investigate the effects of flow coast down and linear decrement of flow for constant corrosion rates [18]. The effects of coolant chemistry were not taken into consideration. Computer code CPAIR was developed in FORTRAN -77, so as to calculate the specific activities due to ^{24}Na , ^{56}Mn , ^{59}Fe , ^{60}Co , and ^{99}Mo in primary circuits of light water reactors. It was shown that the minimum value of coolant activity strongly depends on the slope of the linear decrement of the flow rate. The program was further improved to incorporate the effects of power perturbations on corrosion product activity in the coolants of a PWR [18]. The computer code was then modified as CPAIR-P/PH and the effects of fast and slow transients on dose rates due to corrosion activity in the coolant were studied. All of these studies assumed a constant and uniform corrosion rate and fixed pH values, during and after transients. However, the corrosion rate does increase slowly with plant operation; it also increases with temperature and pressure. The rate of increase in corrosion depends on the integrated effects of the neutron flux, reactor operation cycle length, reactor temperatures and coolant chemistry.

This work is aimed at including the effects of the pH value and chemical shim so as to simulate the behavior of corrosion product activity in a typical PWR over extended cycles. In it, coupled effects of both an increase in the corrosion rate due to normal corroding processes and decreases due to coolant chemistry, are considered in the primary circuit. The said changes were superimposed and the computer program CPAIR [18] modified to incorporate both the linear and non-linear rise in corrosion rates and the effects of pH /boron concentrations in the coolant. Using different coolant pH/chemical shim values, we have first analyzed CPA due to the non-linear accelerating corrosion rates coupled with coolant chemistry effects in an extended operating cycle. The results for various corrosion products of possible pH/boron perturbations are also reported here. Finally, the behavior of time-dependent corrosion product activity using high pH concentrations and enriched boric acid is also presented for multiple long-term operating cycles.

LONG-TERM OPERATING CYCLE AND COOLANT CHEMISTRY

Several studies have shown that the light water reactor's operating cycle can be extended to average batch burn-ups of 45 MWd/kgU for PWR and to about 40 MWd/kgU for BWR. Long-term operating cycles (18-month to 24-month cycles) were shown to increase the capacity factor from 3% to 7%. They also result in an increase of 5 to 7% in fuel fabrication costs, coupled by an overall decrease in the electric power generation costs [1-4].

In general, a 12-month cycle has 1200 ppm of boron at the beginning of the cycle and a maximum of 2.2 ppm of lithium is needed to satisfy the need for a pH value of 6.9 in the primary coolant. However, for a long-term operating cycle of 18-24 months, much higher initial boron in the range of 1500 to 1900 ppm is needed and that puts the pH values in much higher regimes. While on the one hand a higher pH concentration results in an increase in the release rate of various metal ions, on the other, it decreases the solubility of the corrosion product. Both of these effects shape the buildup of corrosion product activity over a long-term operating cycle and, in this work, we have aimed at estimating the said effects of activity buildup. A typical PWR uses natural boric acid (NBA) as a soluble poison or chemical shim. Boron-10 has a very high thermal absorption cross-section (3800 barn); however, natural boron has only a 20 atom percent of B-10, while 80% is B-11 (having a very small absorption cross-section of about 0.005 barn). Several studies have shown that EBA reduces the needed concentration and that an elevated pH value of 7.4 can be used in the coolant with 2.2 ppm of lithium for extended operating cycles [1, 2].

In PWR, along with boron, the level of lithium is adjusted to keep the pH values near 6.9, where the solubility of impurities in the coolant is high. Several studies have indicated that a high value of pH close to 7.4 minimizes nickel ferrite precipitation in the core [1]. Several PWR used lithium at 3.5 ppm and a pH value of 7.4 and have reported lower out-of-core radiation fields. However, elevated lithium programs were interrupted due to concerns over the primary water-based stress corrosion cracking of alloy 600 and zircaloy cladding corrosion due to the prolonged use of lithium at a level of 3.5 ppm.

An extended cycle needs the so-called "modified coolant chemistry" in which the reactor operates with the coolant having a pH value of around 6.9 at the beginning of the cycle with high boron and lithium concentrations, until the lithium drops to 2.2 ppm. At that point, the pH is steadily raised to 7.4 and kept at this value until the end of the cycle, as in the case of enriched boric acid. The trend for possible enrichments of boric acid in a typical PWR, vs. effective full-power days, is shown in fig. 1(a). Also, the pH value as a function of effective full-power days

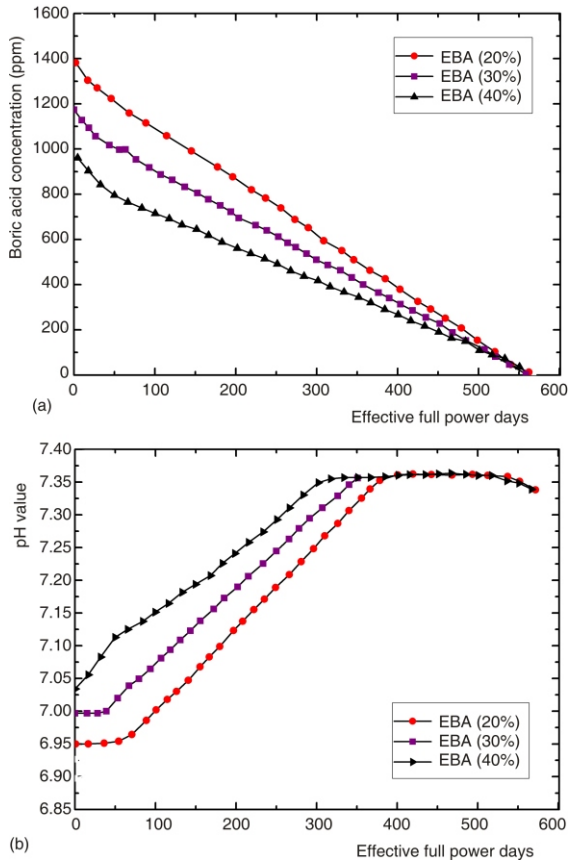


Figure 1. Extended cycle coolant chemistry as a function of time; (a) boron concentration values and (b) pH value of coolant as a function of EFPD for various indicated values of enrichment with soluble boron

(EFPD) is shown in fig. 1(b), pertaining to extended operating cycles [17]. Various possible coolant chemistry scenarios are shown in fig. 1. The first case covers the use of natural boric acid (NBA) in which lithium is kept at a 2.2 ppm level and the initial pH remains close to 6.9. In the second case, enriched boric acid (EBA) of 30% is used: lithium is kept at a less than 2.2 ppm value and pH variations are shown in fig. 1(b). Subsequently, EBA equal to 40% is employed with a Li-concentration value less than 2.2 ppm. The pH variations start at 7.02 and are allowed to increase to 7.35 within approx. 300 days, as shown in fig. 1, respectively.

MATHEMATICAL MODEL

Various pathways leading to the production and losses of corrosion products are shown in fig. 2. We have assumed uniform time-dependent corrosion in the primary coolant circuit and have ignored space distribution effects. The deposition of this activity on surfaces in contact with the cooling water is proportional to the concentration of the corrosion products in water. The concentrations of target nuclides in the primary coolant on the inner walls of the piping and on the core surfaces have been denoted by N_w , N_p , and N_c , respec-

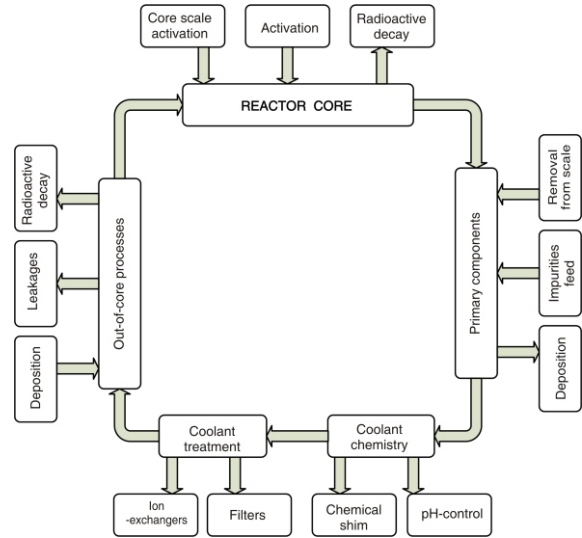


Figure 2. Different paths leading to the production and loss of corrosion products in the primary coolant circuit of a typical PWR

tively, in atoms per cm^3 . Also, the concentrations of the activated nuclides in primary water, on the piping and on the core, have been represented by n_w , n_p , and n_c , respectively, in atoms per cm^3 . In this case, the rate of change of active material concentration in the primary coolant is [20]

$$\frac{dn_w}{dt} = \sigma \phi_\epsilon N_w - \sum_j \frac{\epsilon_j Q_j}{V_w} - \sum_k \frac{l_k}{V_w} - \lambda n_w + \frac{K_p}{V_w} n_p + \frac{K_c}{V_w} n_c \quad (1)$$

where σ is the group constant for the production of the isotope from the target nuclide; ϕ_ϵ is the effective group flux [neutrons per cm^2 per s], N_w is the target nuclide concentration in water [atoms per cm^3]. The values of the decay constant (λ) for each isotope of interest are provided in tab. 1. The sum over j for $\epsilon_j Q_j$ is given as

$$\sum_j \epsilon_j Q_j - \epsilon_I Q_I - \epsilon_p Q_p - \epsilon_c Q_c - \epsilon_F Q_F \quad (2)$$

where, quantities $\epsilon_I Q_I$, $\epsilon_p Q_p$, $\epsilon_c Q_c$, and $\epsilon_F Q_F$ are removal rates due to the ion exchanger, deposition on pipes, deposition on core surfaces and removal by filters, respectively. The term l_k is the rate at which the primary coolant loop loses water from its k^{th} leak [$\text{cm}^3 \text{s}^{-1}$], K_p and K_c are rates at which isotopes are removed from the scale on the piping [$\text{cm}^3 \text{s}^{-1}$] and from the core [$\text{cm}^3 \text{s}^{-1}$], respectively. For a typical PWR, the measured values of these removal rates have been considered [10, 11] and shown in tab. 2. Coolant chemistry change perturbations are introduced through a parameter $h(t)$

$$h(t) = \text{functional dependence of } C(t) \text{ on pH and corrosion rate} \quad (3)$$

The neutron flux for a given energy group is averaged over the geometry of the core and has been esti-

mated using LEOPARD [19] and ODMUG [20] in the CPAIR-P/PH program. The times, T_c and T_L , are the core residence time and loop time (required to complete the primary loop once), respectively, which have been included. The rate of the build-up of target nuclide concentration in coolant water can be written as

$$\frac{dN_w}{dt} = \sum_j \frac{\epsilon_j Q_j}{V_w} - \sum_k \frac{l_k}{V_w} \sigma \phi_\epsilon N_w + \frac{K_p}{V_w} N_p - \frac{K_c}{V_w} N_c + S_w \quad (4)$$

$$S_w = \frac{C(t)S}{V_w} \frac{N_0}{A} f_n f_s \quad (5)$$

where N_p is the concentration of the target nuclide on the piping, N_c is the concentration of the target on the core, and S_w is the source term for corrosion. $C(t)$ is the modified time-dependent corrosion rate [g per cm^2 and s], including the effects of coolant chemistry, S is the area of the system exposed to coolant corrosion, N_0 is the Avogadro's number (6.02×10^{23} atoms per g-mole), and A is the atomic weight of the target nuclide [g]. Here, f_n and f_s , are the abundances of the target nuclide and chemical element in the system, respectively.

The removal of impurity by the ion-exchanger, core deposition and leakage are directly related to the flow rate. Also, the rate of re-entry from the scales is directly proportional to the primary coolant flow rate. Therefore, the rate of activity build-up on the core scale is given by

$$\frac{dn_c}{dt} = \sigma \phi_0 N_c - \frac{\epsilon_c Q_c}{V_c} n_w + \frac{K_c}{V_c} \lambda n_c \quad (6)$$

where V_c is the volume of the scale on the core [cm^3] and ϕ_0 is the thermal neutron flux average over the geometry of the core [neutrons per cm^2 and s]. The rate of build-up of target nuclide concentration on the core scale (N_c) is given by

$$\frac{dN_c}{dt} = \frac{\epsilon_p Q_p}{V_p} n_w - \frac{K_p}{V_p} \delta \phi_0 N_c \quad (7)$$

The rate of deposition of active material on the piping scaling (n_p) can be obtained from the following balance

$$\frac{dn_p}{dt} = \frac{\epsilon_p Q_p}{V_p} n_w - \frac{K_p}{V_p} \lambda n_p \quad (8)$$

where V_p is the volume of scale on the piping [cm^3]. Then, the rate of change of target nuclide on the piping walls (N^p) is

$$\frac{dN_p}{dt} = \frac{\epsilon_p Q_p}{V_p} N_w - \frac{K_p}{V_p} N_p \quad (9)$$

Based on the cited system of equations (1 through 9), the CPAIR-P (corrosion product activity in reactors) computer program [18] was modified to include the effects of both the accelerating corrosion rate and coolant chemistry as functions of time.

The modified CPAIR-P/PH program written for personal computers in FORTRAN-77 now calculates corrosion product activity as a function of reactor operation time under both time-dependent corrosion and coolant chemistry. The overall computational algorithm is illustrated in the form of a flow chart (fig. 3). After initialization, it calculates group constants using core design parameters (tab. 3) in the LEOPARD [19] code which is a zero-dimensional unit cell-based computer code with 54 fast and 172 thermal energy groups. An early data set is used in the cross-section library. In this work, equivalent cells of a typical PWR have been employed to generate group constants for fuel cells and water holes. These cell-averaged group constants are then employed in the one-dimensional multi-group diffusion theory based ODMUG [20] code. Using ODMUG, the group fluxes as a function of position in the reactor are calculated. These group fluxes are subsequently averaged over the core. Both LEOPARD and ODMUG are treated as subroutines of the CPAIR-P/PH program. Then, in next step, equations 1 through 9 are used to find activity values due to corrosion products in the primary coolant, on the piping and core surface.

RESULTS AND DISCUSSION

A typical PWR is considered with the initial concentration of impurities taken to be zero [9]. Experimental data has been employed in the analysis of the fractional exchange rates ($\epsilon_j Q_j / V_q$) and re-resolution rates (K_j / V_q). These values are shown in tab. 2. The de-

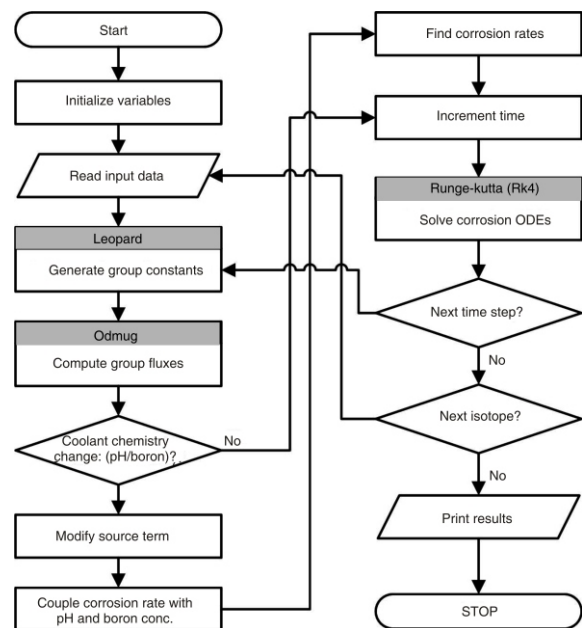


Figure 3. Flow chart of the computer program

sign data values for a typical PWR are shown in tab. 3 [10, 11]. Core averaged group fluxes have been computed using LEOPARD and ODMUG codes. The plant surface area of 10^8cm^2 is exposed to the primary coolant for corrosion and an equilibrium corrosion rate of $2.4 \cdot 10 \text{ g/cm}^2\text{-s}$ [10] exists after a year of reactor operation. It has a primary coolant volume of $1.3 \cdot 10^7 \text{cm}^3$. We assumed values of parameters f_n and f_s as 1.0 and 0.5, respectively, for ^{56}Mn to be on the conservative side. Upon that, a corrosion rate of 25 g/s has been used as a normal equilibrium rate in our subsequent studies.

Table 2. Experimental values of exchange rates in a typical PWR*

Rate type	Value
Deposition on core, $\varepsilon_c Q_c$, [$\text{cm}^3 \text{s}^{-1}$]	80.0
Deposition on piping, $\varepsilon_p Q_p$, [$\text{cm}^3 \text{s}^{-1}$]	13.7
Ion-exchanger removal, $\varepsilon_i Q_i$, [$\text{cm}^3 \text{s}^{-1}$]	500-781
Re-resolution ratio for core, K_c , [$\text{cm}^3 \text{s}^{-1}$]	40.0
Re-resolution ratio for piping, K_p , [$\text{cm}^3 \text{s}^{-1}$]	6.9
Volume of primary coolant, V_w , [cm^3]	$1.37 \cdot 10^7$
Volume of scale on core, V_c , [cm^3]	$9.08 \cdot 10^6$
Volume of scale on piping, V_p , [cm^3]	$1.37 \cdot 10^6$
Total corrosion surface, S , [cm^2]	$1.01 \cdot 10^8$
Average corrosion rate, C_o , [$\text{kg/cm}^2\text{-s}^2$]	$2.4 \cdot 10^{-16}$

* Rafique et al., 2005, and Mirza et al., 2005

Table 3. Design specifications of a typical pressurized water reactor*

Parameter	Value
Specific power [$\text{MWkg}^{-1} \text{U}$]	33
Power density [MWm^{-3}]	102
Core height [m]	4.17
Core diameter [m]	3.37
Assemblies	194
Rods per assembly	264
Fuel type	UO_2
Clad type	Zircaloy
Lattice pitch [mm]	12.6
Fuel rod outer diameter [mm]	9.5
Average enrichment [%]	3.0
Flow rate [kg s^{-1}]	$18.3 \cdot 10^3$
Linear heat rate [kWm^{-2}]	17.5
Coolant pressure [MPa]	15.5
Inlet coolant temperature [$^\circ\text{C}$]	293
Outlet coolant temperature [$^\circ\text{C}$]	329

*Rafique et al., 2005, and Mirza et al., 2005

Simulations are started at time $t = 0$, when the reactor is considered to be operating at full power, without any impurity. The purification rate due to an ion-exchanger, $\varepsilon_i Q_i$, must be large enough to take into consideration deposition, re-resolution and leakage as second-order effects. Therefore, an optimum removal

rate of activity by the ion-exchanger was determined at a constant corrosion rate (25 g/s) and it was found that the saturation value of coolant activity remains fixed when $\varepsilon_i Q_i$ is higher than $400 \text{ cm}^3/\text{s}$. Thus, a removal rate of $600 \text{ cm}^3/\text{s}$ in which the saturation value is sufficiently low was selected.

Five corrosion products (^{56}Mn , ^{24}Na , ^{59}Fe , ^{60}Co , and ^{99}Mo) were considered in this study. Isotope ^{56}Mn remained the largest contributor to the total activity during reactor operation at full power. However, cobalt isotopes dominate coolant activity even after shutdown. Their activity accounts for approx. 36% of the total corrosion product activity in the PWR, whereas other isotopes, including ^{24}Na , ^{59}Fe , ^{99}Mo , and ^{60}Co , contribute with about 23.4%, 29.6%, 9.5%, and 1.4%, respectively. The activity due to ^{56}Mn saturates at about 150 hours after the start of the reactor. Its saturation value is 0.22 Ci/cm^3 and it makes the primary coolant as a 24.531 PBq – source within 150 to 230 hours of reactor operation at full power.

Inclusion of the time-dependent pH value effect

The change in the solubility of a coolant depends on both pH value and temperature. The deposition and release rates of corrosion products depend on solubility. Respective boric acid concentrations [ppm] as a function of EFPD are shown in fig. 1(a) and typical changes of the pH depending on reactor operation time for various EBA are shown in fig. 1(b). Then, the pH level is increased from low to high values in a gradual manner, slowly lowering the solubility. The temperature coefficient of solubility also becomes positive. This translates into a reduction of transport into and out of the core. Also, when the operating cycle period is increased to 24 months, the generation of corrosion products is affected.

We have assumed that the corrosion rate remains constant during the steady-state operation of the reactor and that corrosion product activity for the system is balanced by eqs. 1 through 9. In addition to natural removal by decay and other removal processes, the chemistry of water also affects activity. The said effects on coolant corrosion product activity are observed using the CPAIR-P program. First, we have computed the activity when a constant corrosion rate (25 g/s) is present in the system coupled with time-dependent effects due to pH. Using fig. 1(b), the time-dependent pH for different enrichments of boric acid cases can be written as

$$\text{pH}(t) = \begin{cases} \text{pH}(0); & t_0 \leq t < t_1 \\ \text{pH}(0) + \text{slope} \cdot (t - t_1); & t_1 \leq t < t_2 \\ \text{pH}(0)(\text{max}); & t_2 \leq t < t_{\text{max}} \end{cases} \quad (10)$$

where, t_0 , t_1 , t_2 , and t_{max} are the estimated times from the figure. The slope is calculated using the least

square curve fitting the data. Estimated slopes are 0.00173 per day, 0.00138 per day and 0.00097 per day, for NBA, EBA (30%), and EBA (40%), respectively. Then, the effect on the corrosion rate term with a slope (m) estimated from fig. 1(b) is

$$h(t) = \frac{pH(t) - pH(0)}{pH(max) - pH(0)} \quad (11)$$

The coupled effects of both the constant corrosion rate and the effects of pH on corrosion rate are given by a modified corrosion rate

$$C(t) = h(t)C_{sat} \quad (12)$$

Such a modified corrosion rate has been employed in eq. 4 and 5, respectively, to simulate the build-up of corrosion products in the core, primary coolant and on the inner piping surfaces. For the two cycles, using the above models, the pH-values in the primary coolant as a function of EFPD are shown in fig. 4, for NBA, EBA (30%), and EBA (40%), respectively.

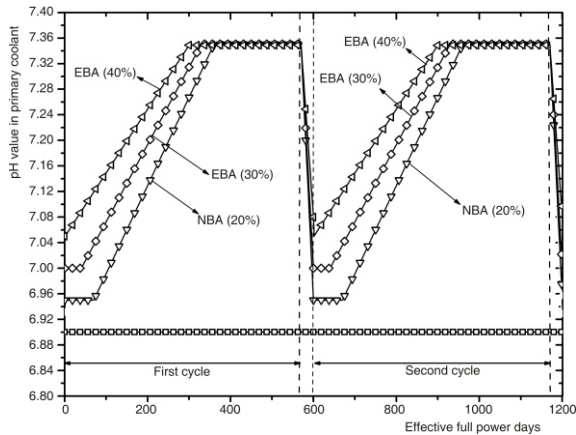


Figure 4. The pH value from model equations for the first two cycles of a typical PWR as a function of EFPD for various enrichment scenarios with soluble boron

Non-linear changes in corrosion and pH effects

A typical PWR can have a non-linear rise of the corrosion rate superimposed by effects of changes in the primary coolant chemistry. We have assumed a linear rise in the corrosion rate, $C(t)$, coupled with pH effects in the coolant with the following model for the first(startup) cycle

$$C(t) = f_{cs} C_s \{1 - \exp[-m(t-a)]\}, \quad a < t < b \quad (13a)$$

$$C(t) = f_{cs} C_s, \quad b < t < c$$

where m is a positive constant slope of the corrosion rate in the time domain $[a, b]$, C_s – the equilibrium value of the rate after time b , $h(t)$ – the effect of time-dependent pH on the corrosion rate as given by eqs. 11 and 12, respectively, and f_{cs} – the fraction of corrosion rate at the end of cycle ($b < t < c$). In this study we have assumed a, b , and c as 10, 570, and 600 days, respectively. For the startup cycle, fig. 5 shows the normalized corrosion rate vs. time for five different cases of soluble boron enrichment (from zero to 40%). If $h(t)$ is taken as one, then the effects due to pH are ignored and EOC corrosion product activity is much larger. The corrosion rate first rises to a peak value and then decreases to a low equilibrium value during the first cycle (fig. 5).

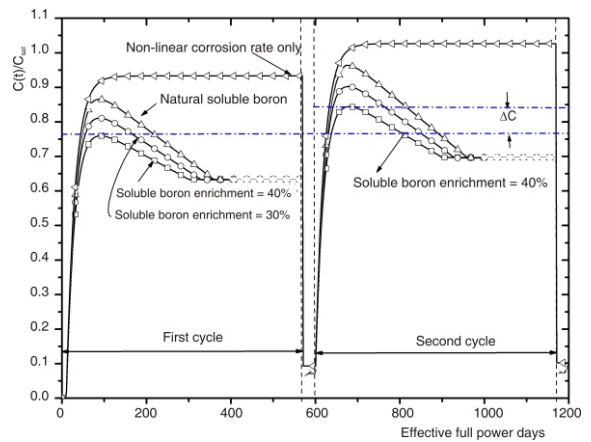


Figure 5. Effective corrosion rate as a function of reactor operation time for various enrichments with soluble boron in the core, primary coolant pipes and primary coolant

In the second burn-up cycle, the corrosion rate $C(t)$ has a non-zero initial value from the first cycle. Then it gets superimposed by the rise in the corrosion rate and a competing decrease in it due to pH. The model for the next cycle is

$$C(t) = \begin{cases} h(t)[f_{cs} C_s - C_s \{1 - \exp[-m(t-c)]\}], & c < t < d \\ h(t)f_{cs} C_s, & d < t < e \end{cases} \quad (13b)$$

For the second cycle, we have taken values of c, d , and e as 600, 1170, and 1200 days, respectively. The normalized corrosion rate vs. time for an equilibrium value (C_s) using the above model for NBA, EBA(30%), and EBA(40%), respectively, is shown in fig. 5. Here, the EOC equilibrium corrosion rate value for the second cycle ($0.696 C_s$) is higher compared to the equilibrium value for the first cycle ($0.633 C_s$). The ΔC shown in the figure is about $0.084 C_s$ in the case of 40% enriched boric acid. In the second cycle, the corrosion rate rises again to a maximum value and then starts decreasing due to pH effects and gains a new equilibrium value, as shown in fig. 5.

Using corrosion rates shown in fig. 5, the specific activity for ^{60}Co from the modified CPAIR-P/PH

code as a function of time for the core, pipes and primary coolant is shown in fig. 6. The study has been carried out for various boron concentration scenarios that in turn change the pH values in the primary coolant. When we consider $h(t) = 1$ (no effect of pH-value on corrosion) then, first, only a non-linear rise in corrosion occurs and it saturates to an equilibrium value. These values are the largest of all cases for the core, pipes, and coolant regions. In the first cycle, the saturation values are 8.88 kBq/cm³, 3.7 kBq/cm³, and 0.629 kBq/cm³ for core, primary pipes and coolant, respectively.

In all other cases with natural or enriched boron in the primary coolant, the activity in the first hundred days builds up and eventually saturates within the core region. Then, due to an increase in pH value from pH(0) to pH(max) in steps, a decrease in the corrosion rate occurs and the resulting ⁶⁰Co activity also starts decreasing monotonically (fig. 6). As soon as the pH reaches the high value of pH(max), the activity attains a new low saturation value. This effect is further pronounced when we test the plant for enriched boric acid and a different set of values for the rate of increase of pH values is employed. As the pH increases and the corrosion rate decreases, dictated by the gain and loss terms in the balance equations, the end of cycle activity then becomes much lower when compared with values in a case where $h(t) = 1$. This saturation can be achieved much earlier in case of EBA (40%) than NBA. Similarly, in the primary pipes, the end of cycle activity for NBA is about 50% lower when compared with the $h(t) = 1$ case. When we use 40% EBA, an earlier saturation (within 300 days) occurs to these low activity values.

For the non-linear rise in the corrosion rate, in case of EBA (40%), the specific activity in the primary coolant reaches the equilibrium value in the shortest time of all cases (tab. 4). The peak value in the second cycle is higher when compared with peak values in the first cycle. The equilibrium or saturation CPA values are also higher for the second cycle, as compared to the values in the first cycle for all three regions. The equilibrium values for EBA (40%) in the first cycle are 6.068 kBq/cm³, 2.627 kBq/cm³, and 0.444 kBq/cm³ in the core, primary pipes and coolant regions, respectively.

These values are 46%, 41%, and 42% lower when compared with equilibrium values for $h(t) = 1$ for all three regions, respectively. The overall behavior of CPA shows an initial rise in the activity that reaches a peak value due to the rise in the corrosion rate and then falls to a low saturation value, due to coolant chemistry effects.

The short-lived ⁵⁶Mn (half-life ~2.58 hours) dominates the total specific activity due to corrosion products. The specific activity due to ⁶⁰Co (half-life ~5.3 year) remains low during burn-up cycles; however, it dominates after reactor shutdown. Its EOC value decides the total activity after reactor outage. In the case of EBA (40%), we have compared the specific activity due to ⁵⁶Mn and ⁶⁰Co for two cycles and the results are shown in fig. 7. In the first cycle, the saturation values for core, pipe and coolant are 387.02 kBq/cm³, 4.625 kBq/cm³, and 3.737 kBq/cm³, respectively, for ⁵⁶Mn. However, due to ⁶⁰Co, the values are 6.068 kBq/cm³, 5.18 kBq/cm³, and 0.148 kBq/cm³ in the three regions, respectively. During the reactor shutdown period (570 days < t < 600 days), ⁵⁶Mn activity becomes less than 10⁻⁵ kBq/cm³ and ⁶⁰Co activity remains at levels of

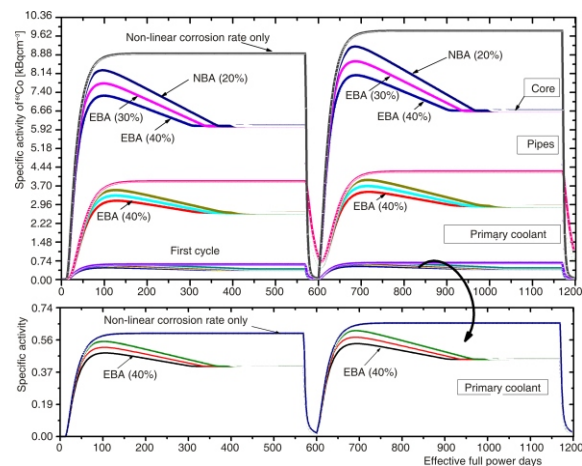


Figure 6. Specific activity due to ⁶⁰Co in the core, primary pipes and the primary coolant of a PWR under different enrichments of soluble boron and pH scenarios. Here, the non-linear corrosion rate only case means $h(t) = 1$ (no effect of pH-value)

Table 4. Equilibrium and peak values for ⁶⁰Co specific activity kBq/cm³ (μCi/cm³) for two cycles

Case	Core	Primary pipes	Primary coolant
First cycle equilibrium value	6.068(0.164)	2.627(0.071)	0.407(0.011)
Second cycle equilibrium value	6.697(0.181)	2.886(0.078)	0.444(0.012)
First cycle peak:			
NBA (20%)	8.288(0.224)	7.067(0.191)	0.5476(0.0148)
EBA (30%)	7.77(0.210)	6.66(0.180)	0.518(0.0140)
EBA (40%)	7.252(0.196)	6.253(0.169)	0.481(0.0130)
Second cycle peak:			
NBA (20%)	9.213(0.249)	7.881(0.213)	0.6068(0.0164)
EBA (30%)	8.621(0.233)	7.4(0.200)	0.5698(0.0154)
EBA (40%)	8.066(0.218)	6.919(0.187)	0.5328(0.0144)

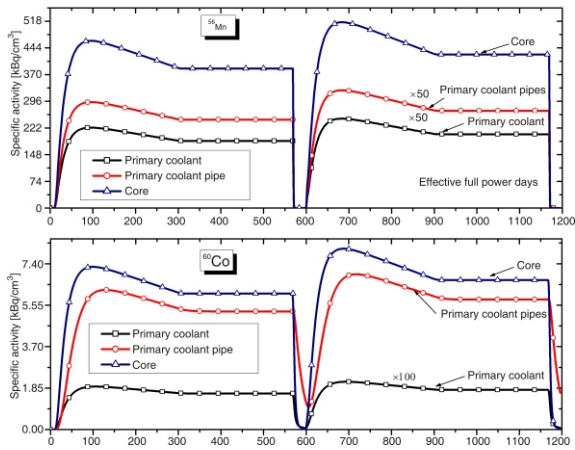


Figure 7. Comparison of the specific activity due to ^{56}Mn and ^{60}Co for the core, primary pipes, and primary coolant with a non-linearly rising corrosion rate and EBA (40%) in the first two extended cycles

0.0037, 1.48, and 0.148 kBq/cm^3 for the three respective regions. Cobalt isotopes remain the largest contributors even after reactor shutdown and its saturation values are the lowest in the EBA (40%) scenario, even with the non-linear rise in the corrosion rate. These results were compared with the reported results of the COTRAN code [17] and our results are in good agreement with end-of-cycle behaviors and values for similar extended cycles. The results by Song *et al.* [17] for extended multiple cycles showed a linear increase in CRUD and a non-linear rise in core activity.

We have also compared corrosion product activity due to the ^{60}Co in the core, pipes, and primary coolant for multiple long-term operating cycles. This analysis was done for EBA (40%) where the lowest peaks occur and relatively quick equilibrium is achieved. The results of the three-cycle analysis are shown in fig. 8. For the core region, the peak value in the second cycle is about 11% higher when compared to the peak value in the first cycle. The value of the third cycle peak is only 1% higher than the second peak. Similar results are obtained for pipes and coolant. They show that no substantial increase in the peak or saturation values occurs after the second cycle. Thus, the EOC values of the second cycle can be used to represent the saturation value for the equilibrium core. The saturation values in each cycle also remain a function of the performance index ($\varepsilon_1 Q_1$) of the ion-exchanger. Here, we have assumed the removal rate from the ion-exchanger as $\varepsilon_1 Q_1 \sim 600\text{-}900 \text{ cm}^3/\text{s}$. If the removal rates of the ion-exchanger are low ($\varepsilon_1 Q_1 \sim 100\text{-}300 \text{ cm}^3/\text{s}$), then the activity keeps building up and in subsequent cycles saturation values become gradually higher. However, when ion-exchanger performs well ($\varepsilon_1 Q_1 \sim 600\text{-}900 \text{ cm}^3/\text{s}$), then the overall ^{60}Co activity remains low and the saturation value does not grow much in subsequent cycles.

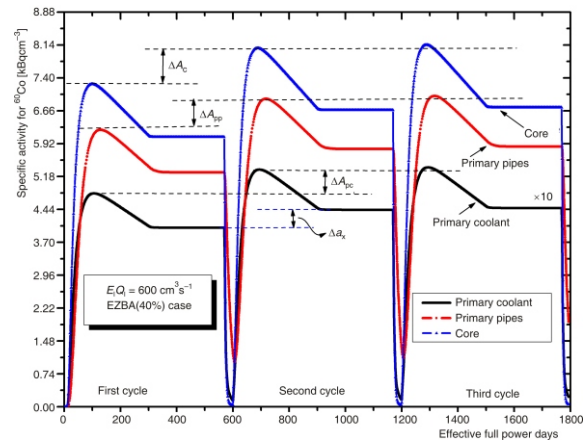


Figure 8. Comparison of the specific activity due to ^{60}Co in the first three cycles having a non-linearly rising corrosion rate and EBA (40%) within the core, primary pipes, and primary coolant of a typical PWR

CONCLUSIONS

The shift of nuclear power plant operation practice from a 12-month operating cycle to 18-24 months long-term operating cycles requires new operational methods to satisfy long-term safety and protection. These extended operating cycles have complicated effects on primary coolant chemistry and finding the optimum pH concentration range. From the results of the modified CPAIR-P/PH code, it has been observed that for ^{24}Na , ^{56}Mn , ^{59}Fe , ^{60}Co , and ^{99}Mo , the specific activity in the primary loop approaches equilibrium values under normal operating conditions fairly rapidly. During reactor operation, the predominant corrosion product activity is due to ^{56}Mn and post-shutdown activity due to the dominance of cobalt isotopes. The pH values and the operating cycle length are key factors affecting corrosion product activity in the core region, primary pipes, and primary coolant.

These simulations suggest that the effects on the specific activity of an increase in pH value for an extended 24 month cycle, in the form of a decrease in the activity, is smeared by the non-linearly rising corrosion rate. The new saturation values for activity at the end of the cycle are lower than the corresponding values for a reactor operated at a constant low pH/natural boric acid in the coolant. As for the non-linear rise in the corrosion rate coupled with a rise in pH from 6.9 to 7.4 and the use of enriched boric acid (10% - 40%), this results in a coolant activity peak during the cycle, dropping to much smaller saturation values at the end of the cycle, when compared with the activity of the system having a constant low pH value (6.9) in the coolant. The use of enriched boric acid as a chemical shim actually lowers the primary coolant activity when, rather than natural boric acid, higher pH values are employed in the coolant. For multiple long-term

operating cycles, the saturation value of corrosion product activity increases in the first two cycles and then becomes constant in next cycle due to the high pH concentration for the enriched boric acid (40%) used as chemical shim.

ACKNOWLEDGEMENT

Javaid I. Malik gratefully acknowledges the financial support of the Higher Education Commission (HEC), Pakistan, for the Ph. D. (Indigenous) Fellowship under scholarship No. 074-1458-Ps4-407 /HEC/Ind-Sch/2007.

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Received on November 29, 2011

Accepted on May 29, 2012

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**ПРОУЧАВАЊЕ АКТИВНОСТИ ПРОИЗВОДА КОРОЗИЈЕ, У PWR
РЕАКТОРИМА СА ПРОДУЖЕНИМ ГОРИВНИМ ЦИКЛУСИМА**

Овај рад је студија о променама у активности расхладне течности услед корозионих продуката продуженог горивног циклуса у трајању од 18-24 месеца у типичном PWR реактору, са варијацијама вредности рН и борне киселине. Разматра се нелинеарна промена брзине корозије повезана са рН ефектима измењеним рачунарским програмом SPAIR-P прилагођеним временски зависном расту корозије и хемијским ефектима у расхладној течности. Симулације сугеришу да је ефект пораста рН вредности у продуженом двогодишњем циклусу у облику смањења специфичне активности – ублажен растом корозије. Нове вредности засићења активности на крају циклуса ниже су од оних када реактор ради при константно ниској вредности рН и са природним стањем борне киселине у расхладној течности. За нелинеарни пораст брзине корозије повезан са порастом рН вредности са 6.9 на 7.4 и уз употребу обогаћене борне киселине (30%–40%), активност расхладне течности најпре расте до максималне вредности током циклуса и потом се приближава знатно мањој сатурационој вредности на крају циклуса – у поређењу са активношћу система код кога је вредност рН у хладиоцу константно ниска (6.9). У овом раду показано је да употреба обогаћене борне киселине у хладиоцу, уместо природне борне киселине као хемијске подлоге, смањује активност примарне расхладне течности када су веће рН вредности. За вишеструке дуготрајне циклусе, сатурациона вредност активности корозионих продуката расте у прва два циклуса и постаје константа у наредним циклусима услед високе радне рН вредности обогаћене борне киселине (40%) као хемијске подлоге.

Кључне речи: моделовање и симулација на рачунару, производ корозије, рН вредности, обогаћена борна киселина, PWR реактор, продужени горивни циклус
