THE ELECTROCHEMISTRY OF WATER-COOLED NUCLEAR REACTORS

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Corrosion is a major cause of unscheduled down time in the nuclear power industry, with losses of up to \$3 million per day being incurred for a large (1000 MW) unit. The forms of corrosion that are experienced range from wastage and flow-assisted corrosion to pitting attack, stress corrosion cracking, nodular attack (on Zircaloy fuel cladding), hydrogen-assisted cracking (HIC), and corrosion fatigue. Each of these processes has an associated critical electrochemical potential (ECP), below or above which the phenomenon occurs. For example, HIC in Alloy 600 occurs at potentials that are more negative than the critical value, whereas IGSCC (Intergranular Stress Corrosion Cracking) of sensitized Type 304 SS occurs only at potentials that are more positive than the critical value.



Figure 1: Variation of the calculated ECP around the heat transport circuit of a BWR operating at full power under normal water chemistry (NWC) and moderate hydrogen water chemistry (HWC) conditions (1.2 ppm of hydrogen in the reactor feedwater).

Clearly, if the ECP and the critical potential are known throughout the heat transport circuit (HTC) the chemistry of the system may be engineered so as to avoid many of the more deleterious forms of corrosion. However, the heat transport circuits of nuclear power reactors are extraordinarily harsh hydrothermal and radiochemical environments, due to the high operating temperatures [up to 340 °C for Pressurized Water Reactors (PWRs) and 288 °C for Boiling Water Reactors (BWRs)] and the presence of intense radiation fields in the core, so that even the simplest electrochemical measurements (e.g., measurement of ECP) are difficult, if not impossible, to perform. As an alternative to direct measurement of ECP, we have developed a variety of radiolytic/electrochemical models that can be used to predict with remarkable accuracy the ECP around the entire HTC if the thermal hydraulic properties of the system are known.





Figure 2. Calculated corrosion potential (ECP) vs. distance for the fuel channels and core by-pass in a PWR under full power operation. S1 = RPV entrance, S2 = Core channels (fuel rods), S3 = Hot assembly (fuel bundle), S4 = RPV head, S5 = By-pass tube guide, S6 = By-pass cavity, S7 = By-pass grid. $[H_2] = 25 \text{ cc}(\text{STP})/\text{kg}$, [B] = 840 ppm and [Li] = 1.9 ppm, under full power conditions, with $[O_2] = 5 \text{ ppm}$ in the feedwater.

As examples of these calculations, we show in Figure 1 predicted ECP as a function of distance along the flow path for a BWR operating at full power (T = 288 °C) under normal water chemistry (NWC) and hydrogen water chemistry conditions. In the latter case, 1.2 ppm of H₂ was added to the reactor feedwater. As seen in these figures, the ECP of many components are displaced in the negative direction, thereby reducing the driving force for IGSCC in sensitized Type 304 SS. However, other regions are little affected, either because the intense radiation field swamps any impact of hydrogen or because boiling in the core strips the hydrogen from the local environment.

Figure 2 shows calculated ECP for the core region of a PWR operating at full power with the coolant (840 ppm B as boric acid + 1.9 ppm Li as LiOH) at 340 °C and with a coolant hydrogen concentration of 25 cc(STP)/kg. The very high hydrogen concentration displaces the ECP of the non-boiling core to values that are much more negative than those in the core of a BWR, despite the fact that the radiation fields are much higher in the former than in the latter.

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