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Modeling the critical hydrogen concentration in the AECL test reactor

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HIGHLIGHTS

- Hydrogen is added to nuclear reactor cooling loops to prevent radiolysis.
- Tests at AECL were carried out to determine the critical hydrogen concentration.
- Neutron radiolysis G-values need to be modified to understand the results.
- Ammonia impurity needs to be included for quantitative modeling.

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ABSTRACT

Hydrogen is added to a pressurized water reactor (PWR) to suppress radiolysis and maintain reducing conditions. The minimum hydrogen concentration needed to prevent radiolysis is referred to as the critical hydrogen concentration (CHC). The CHC was measured experimentally in the mid-1990s by Elliot and Stuart in a reactor loop at Atomic Energy of Canada (AECL), and was found to be approximately 0.5 scc/kg for typical PWR conditions. This value is well below industry-normal PWR operating levels near 40 scc/kg. Radiation chemistry models have also predicted a low CHC, even below the AECL experimental result. In the last few years some of the radiation chemical kinetic rate constants have been re-measured and G-values have been reassessed by Elliot and Bartels. These new data have been used in this work to revise the models and compare them with AECL experimental data. It is quite clear that the scavenging yields tabulated for high-LET radiolysis by Elliot and Bartels are not appropriate to use in the present context, where track-escape yields are needed to describe the homogeneous recombination kinetics in the mixed radiation field. In the absence of such data for high temperature PWR conditions, we have used the neutron G-values as fitting parameters. Even with this expedient, the model predicts at least a factor of two smaller CHC than was observed. We demonstrate that to recover the reported CHC result, the chemistry of ammonia impurity must be included.

1. Introduction

Radiolysis of water in pressurized water reactor (PWR) coolant produces a set of short-lived reactive radicals (H•, e^-_{aq} and OH•) and long lived molecular products (H_2 and H_2O_2) (Draganic and Draganic, 1971; Elliot and Bartels, 2009; Elliot and Stuart, 2008; Spinks and Woods, 1990). In order to prevent the buildup of H_2O_2 and its decomposition product O_2, H_2 is added to PWR coolant at concentrations of 30–40 scc/kg (1200–1600 micromolal) (Millet, 1999). Reaction R32b of OH• with excess H_2 (reaction numbering scheme is taken from (Elliot and Bartels, 2009))

$$OH\bullet + H_2 \rightarrow H\bullet + H_2O \qquad \text{(R32b)}$$

converts the oxidizing OH• radical to the reducing H• atom, and ensures that reducing conditions are maintained within the coolant, which is important for the prevention of stress corrosion cracking (Was et al., 2011).

There are concerns that the current PWR hydrogen level gives the maximum SCC growth rate of Inconel for reducing conditions (Morton et al., 1999; Totsuka et al., 2000). Therefore there is now a debate as to whether to increase or decrease the current hydrogen concentration to reduce the risk from stress corrosion cracking. However, too much hydrogen may cause problems; in boiling water reactors it leads to ^{16}N carryover in the steam lines (Lin, 2009) and in PWRs it may lead to increased levels of soluble iron, nickel and particulate material in the water, giving fuel crud deposition and high ex-core activity levels (Armstrong et al., 1999). Decreasing the amount of hydrogen may give unacceptable levels of oxidants. Knowing the minimum hydrogen level required by the plant to suppress radiolysis is therefore

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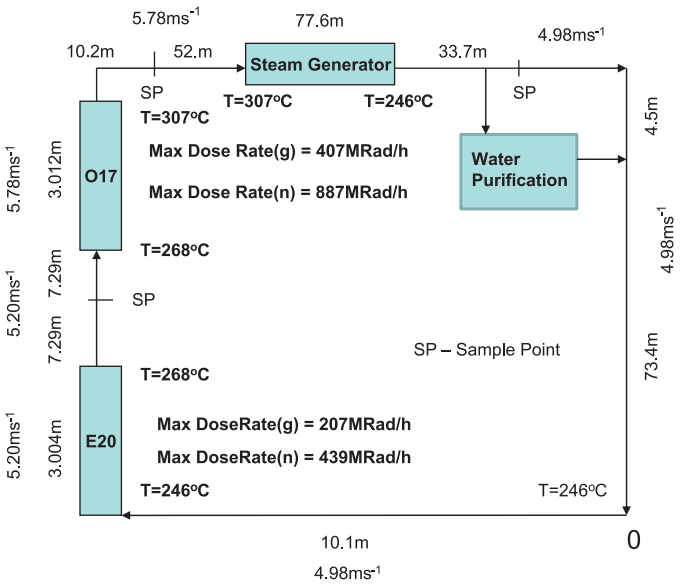

Fig. 1. Schematic representation of the AECL U2 test loop used to define the model. Section distances are indicated in meters and velocity in various sections is indicated in m s^{-1}.

important. There are also practical economic issues associated with operating at the minimum hydrogen level, as this may shorten the period for shutdown and start-up, as well as minimizing the amount of H_2 purchased.

The amount of hydrogen required to suppress the production of oxidants by water radiolysis in these reactors is uncertain. The levels of H_2 currently used were estimated many years ago and were based on laboratory and modeling studies at low temperatures before the temperature dependence of the radiation chemical reactions had been measured. The accepted minimum value of 10–15 scc/kg was first reported in the open literature in an overview chapter by Solomon (1978), who quoted unreferenced modeling work by Fletcher. The results are shown in Fig. 1 of Solomon, but no information is given on the boron concentration assumed, which could influence the result due to recoil ion radiolysis from the $^{10}B(n, \alpha)^7Li$ reaction.

Since the early work, the amount of H_2 required to suppress net radiolytic decomposition of water has been shown to be somewhat less than 10–15 scc/kg H_2, by test loop measurements at AECL discussed in this report (Elliot and Stuart, 2008), tests at the Belleville reactor (Brun et al., 1994), Bruce CANDU (heavy water) reactor (Elliot and Stuart, 2007), and tests by Pastina et al. (1999). In a companion paper, new experiments at Notre Dame Radiation Lab determined the critical hydrogen concentration up to supercritical water conditions for the case of pure low-LET radiation from an electron accelerator (Kanjana et al., 2012). In addition to the experimental tests, there has been a significant amount of new modeling work suggesting that the critical hydrogen concentration is well below 10–15 scc/kg. The modeling studies require experimental data on the kinetics of radiolysis reactions in water at high temperatures. The most recent chemical kinetic data have been obtained at temperatures >300 °C as part of a series of measurements (Cline et al., 2002; Hare et al., 2010; Janik et al., 2007a, 2007b, 2007c; Marin et al., 2003a, 2003b; Marin et al., 2005; Marin et al., 2007; Stanisky et al., 2010) on supercritical water from Argonne National Laboratory (ANL) and the Notre Dame Radiation Laboratory, and a similar series of experiments at the University of Tokyo (Lin et al., 2004, 2005, 2008).

The kinetic data and radiolytic yields have recently been reassessed by Elliot and Bartels (2009) and this paper describes the use of the recommended parameters to model an AECL experimental water loop incorporated into the NRU test reactor at Chalk River, Canada (Elliot and Stuart, 2008). The loop was operated initially under reducing conditions, i.e. excess of H_2; H_2 was then gradually removed and the point at which net radiolysis started was measured. This is referred to as the critical hydrogen concentration (CHC) and was found to be less than 1 scc/kg H_2. The modeling work reported here aims to examine whether current models for the radiolysis chemistry of water are consistent with this observation, and the extent to which the predictions of the model are sensitive to the various chemical rate constants used.

2. Model

The U2 test loop of the Chalk River NRU reactor and the experimental results from the AECL study are described in detail in (Elliot and Stuart, 2008). In summary it consists of a recirculating water loop of mainly stainless steel pipe-work but with two Zr-2.5%Nb test sections within the NRU reactor core. The volume of water in the loop was approximately 935 dm^3 and the loop was operated at $pH_{25\ °C}=10–10.4$. Fig. 1 is a representation of the loop used to define the input parameters for the model.

The labels for the in-core test sections E-20 and O-17 are those adopted in (Elliot and Stuart, 2008). In the first test section (E-20), the water flow is vertically down, while in the second test section (O-17), the flow is vertically up. During passage through the core the water is heated to 307 °C and is cooled via a heat exchanger (SG) down to 246 °C for recirculation back to the first core test section. Velocity of the water (m s^{-1}) is indicated for the various loop sections in Fig. 1 along with the length of each section. The overall loop is nearly 200 m long and the total loop recirculation time is approximately 50 s. Each in-core test section is roughly 3 m in length; time for the water to pass through each test section is on the order of half a second.

The power profiles in the two test sections were reported by AECL (Donders and Elliot, 2009; Elliot and Stuart, 2008). The maximum dose rates for neutron (n) and gamma (g) in each of the sections are indicated in Fig. 1. The relative power profiles were fitted to a polynomial of the form

$$\text{Relative Dose Rate} = \sum_{i=o}^{7} a_i x^i \quad (1)$$

where x is the distance from the center of the test section and the polynomial coefficients were provided in (Donders and Elliot, 2009). The absolute dose rate at position x was obtained for the model calculation by multiplying the relative dose rate by the maximum value. It should be noted that the neutron/gamma dose rate ratio is roughly 2:1 for the numbers given in Fig. 1. The original ratio given in (Elliot and Stuart, 2008) was much closer to 1:1, but was revised in a subsequent AECL analysis (Donders and Elliot, 2009). The neutron numbers remained essentially the same, but the gamma dose was revised downward. The gamma dose estimate remains uncertain by about 30%.

In the core it can be reasonably assumed that gamma and neutron dose rates are proportional (Donders and Elliot, 2009; Elliot and Stuart, 2008). This will not be true at the entrance and exit of the test sections because of the difference in neutron and gamma stopping powers. The dose rate profile was extended into the regions immediately adjacent to the in-core test sections assuming exponential decay of the gamma and neutron fluxes into these regions. In these areas the dose rates are therefore given by expressions of the form

$$\text{Dose Rate} = R_o \exp(-\beta x) \quad (2)$$

where R_o is the dose rate at the end of the irradiated test section given by Donders and Elliot, x is the distance away from the