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# Electrochemical Corrosion of Zircaloys Under Irradiation and Different Water Chemistry Conditions

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***ABSTRACT:*** Shadow corrosion is observed in BWRs either on fuel cladding in contact with Inconel spacers or on channel in close proximity to 304 SS control blades. In order to understand the shadow corrosion mechanism, electrochemical corrosion behavior of Zircaloy-2, Alloy X-750 and 304 SS were previously investigated under UV radiation and published previously. In this study, effects of radiation (up to 300 keV photons) and water chemistry on the electrochemical corrosion behavior of Zircaloy-2, Alloy X-750, and 304 SS were investigated. Measurements of corrosion potential, galvanic corrosion and electrochemical impedance were carried out in 0.01M $Na_2SO_4$ at 25 ºC under UV illumination at 5 eV or photon energies from 2.5 keV to 300 keV using synchrotron radiation. Also, similar measurements were performed in high purity water under various water chemistry conditions at 290 ºC – 300 ºC by using UV illumination. The results show that the presence of radiation shifted the corrosion potential of Zircaloy-2 and Alloy X-750 in the anodic or cathodic direction, respectively, and increased anodic currents when Zircaloy-2 was galvanically coupled with Alloy X-750 in 0.01M $Na_2SO_4$ at 25 ºC, may cause accelerated corrosion of Zircaloy-2. In addition, the results showed that hydrogen peroxide increased the electrochemical kinetics at Zircaloy-2 surface in high temperature water under UV irradiation.

***KEYWORDS:*** *shadow corrosion, electrochemical properties of Zircaloys, channel shadow corrosion, enhanced spacer shadow corrosion, water chemistry, low energy radiation, synchrotron*

## I. INTRODUCTION

When Zircaloy is placed in close proximity to dissimilar metals, such as SS and Alloy X-750, local accelerated corrosion is formed on Zircaloy only on the regions close to dissimilar metals under irradiation in an oxidizing environment, such as in BWR cores. This phenomenon is called "shadow corrosion", since the local accelerated corrosion layer may display the shape of the dissimilar metal components [1-3]. Shadow corrosion is not a new phenomenon and has been observed only in BWR environments for many years. Enhanced shadow corrosion underneath Alloy X-750 spacers resulted in fuel failures in a BWR in late 1990s [4]. It also has been reported that excessive deformation of the fuel channel can result in the interference between the fuel channel and the control blade motion and it is believed to be due to the difference in hydrogen pickup between the opposing side of the channel [5, 6].

Several mechanisms have been proposed to explain the shadow corrosion mechanism, and the majority of them are related to electrochemical nature of the Zircaloys. An extensive study was performed to investigate the photelectrochemical corrosion characteristics of Zircaloy under UV illumination by measuring corrosion potential, oxide impedance, and galvanic corrosion behavior and published previously [7, 8]. As part of that study, this paper is focused on how the electrochemical behavior of Zircaloy changes under X-ray radiation as well as specific radiolysis particles under UV illumination.

Under the oxidizing water chemistry condition, UV illumination increases the galvanic current of Zircaloy-2 coupled to Alloy X-750 and decreased to the oxide impedance of zirconium oxide [7]. This result indicates increased susceptibility of Zr-alloys to galvanic corrosion when in contact with Alloy X-750 under UV radiation. It is not known if this effect will change with higher energy radiation.

The primary chemical effect of radiation is known to form the free radicals which also react with one another, to some extent, to form $H_2$, $O_2$, and $H_2O_2$. The concentrations of the free radicals can be calculated by radiolysis models [9, 10]. The primary products must be in chemical and charge balance. Some of the radicals escape from the radiolysis zone and react with dissolved $H_2$, $O_2$, and $H_2O_2$ molecules in the solution to lead the reformation of water. Thus, the radiolysis products would alter the redox chemistry and might change the kinetics of both the initiation and propagation of electrochemical processes. The radiation-induced water decomposition can be expressed by

$$H_2O \rightarrow e^-_{aq}, OH, H_2O_2, O_2, H, H_2, H^+ \quad (1)$$