



## Effects of $\gamma$ -radiation versus $\text{H}_2\text{O}_2$ on carbon steel corrosion

K. Daub, X. Zhang, J.J. Noël, J.C. Wren\*

Department of Chemistry, the University of Western Ontario, 1151 Richmond St., London, ON, N6A 5B7 Canada

### ARTICLE INFO

#### Article history:

Received 1 October 2009  
 Received in revised form  
 11 December 2009  
 Accepted 12 December 2009  
 Available online 29 December 2009

#### Keywords:

Carbon steel  
 $\gamma$ -Irradiation  
 Peroxide  
 Corrosion potential  
 Polarization resistance

### ABSTRACT

The effect of ionizing radiation on steel corrosion is an important materials issue in nuclear reactors. In the presence of ionizing radiation water decomposes into both oxidizing and reducing species (e.g.,  $\cdot\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\cdot\text{O}_2^-$ ) whose net interactions with steels are not fully understood. The effect of radiation on the corrosion kinetics of carbon steel has been studied at pH 10.6 and room temperature, using electrochemical and chemical speciation analyses. The present study investigates the effect of  $\gamma$ -radiation on carbon steel corrosion and compares it with that of chemically added  $\text{H}_2\text{O}_2$ , which is considered to be the key radiolytically produced oxidant at room temperature. Various oxide films were pre-grown potentiostatically on carbon steel electrodes, and then exposed to either  $\gamma$ -radiation at a dose rate of  $\sim 6.8 \text{ kGy h}^{-1}$  or to  $\text{H}_2\text{O}_2$  in a concentration range of  $10^{-6}$  to  $10^{-2}$  M. The corrosion kinetics were studied by monitoring the corrosion potential ( $E_{\text{CORR}}$ ), and periodically performing linear polarization (LP) and electrochemical impedance spectroscopy (EIS) measurements.

© 2009 Elsevier Ltd. All rights reserved.

### 1. Introduction

Accurate understanding of the effects of ionizing radiation on nuclear reactor system chemistry and materials corrosion is important for assessment of various operational and maintenance requirements and safety margins of nuclear power plants. Exposed to ionizing radiation (e.g.,  $\gamma$ -radiation), water decomposes into both oxidizing and reducing species, such as  $\cdot\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\cdot\text{O}_2^-$ , etc., whose net interactions with steels are not well characterized. In a constant radiation field, these radiolysis products achieve low, but steady-state levels and can dictate the aqueous redox condition, and, hence, may control corrosion reactions. However, since the radiolysis products are chemically reactive, their steady-state concentrations in the homogeneous solution phase can be easily affected by features of the aqueous chemical environment such as pH, temperature and the presence of other dissolved species. For example, during  $\gamma$ -radiolysis of water, there is an increase of more than two orders of magnitude in the production of  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  when the pH increases from 6.0 to 10.6 [1,2]. Oxide film formation and conversion on carbon steel, and hence, the corrosion rate, are also strongly pH and potential-dependent [3]. This potential dependence of the carbon steel corrosion varies considerably with pH. Consequently, the net effect of water radiolysis on metal corrosion and corrosion product transport is often difficult to predict.

The influence of ionizing radiation on corrosion of metals in general, and, of carbon steel in particular, has been studied only to a limited extent, and the mechanism by which radiation affects corrosion kinetics has not been established [4–8]. The observed effects of ionizing radiation on the corrosion of metals are conflicting [4–15], and many key questions remain unanswered, including whether the radiation energy initially absorbed in the bulk metal phase, or that in the aqueous phase, is what drives materials degradation, and whether the key aqueous redox species for steel corrosion are the radical products or the molecular products from water radiolysis.

Previous studies on the effect of  $\gamma$ -radiation reported that the corrosion of carbon steel is enhanced by radiation exposure. However, most of these studies relied on very limited measurements such as the amounts of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  ions released to the solution and later collected by filtration [4,5] or on the weight loss of test coupons [6–8]. Electrochemical methods of monitoring surface changes during corrosion were not employed by these authors. Although the possibility that radiation-induced oxidation of dissolved  $\text{Fe}^{2+}$  ions is the dominant effect was also raised [2], these studies did not probe the role of water radiolysis products as redox agents that may dictate the film formation and conversion on carbon steel. Only Fujita et al. [7,8] attempted to examine the types of corrosion deposits formed on the metal surfaces, finding only magnetite by X-ray diffraction under their exposure conditions.

To develop a fundamental understanding of the effects of water radiolysis on system chemistry and materials degradation in nuclear reactor environments, a comprehensive program has been put in place, which includes studies on catalytic effects

\* Corresponding author. Tel.: +1 519 661 2111x86339; fax: +1 519 661 3022.  
 E-mail address: [jcwren@uwo.ca](mailto:jcwren@uwo.ca) (J.C. Wren).

of dissolved chemical additives (corrosion products and pH- or redox-controlling agents) on water radiolysis and steel corrosion in aggressive redox environments that simulate radiolytically induced aqueous environments by chemical additions, as well as steel corrosion in a  $\gamma$ -irradiation field.

This study investigates the effects of  $\gamma$ -radiation on carbon steel corrosion and compares them with those of chemically added  $H_2O_2$  that is considered to be the key radiolytically produced oxidant at room temperature. The corrosion kinetics are monitored by measuring the corrosion potential,  $E_{CORR}$ , and the polarization resistance,  $R_p$ , using linear polarization (LP) and electrochemical impedance spectroscopy (EIS). Since surface morphology and composition, in addition to the change in the aqueous redox environment induced by  $\gamma$ -irradiation, are important factors controlling the corrosion rate, this study has been performed with various oxide films that were pre-grown potentiostatically on carbon steel electrodes prior to exposure to either  $\gamma$ -radiation at a dose rate of  $\sim 6.8 \text{ kGy h}^{-1}$  or to  $H_2O_2$  at concentrations in the range of  $10^{-6}$  to  $10^{-2} \text{ M}$ .

## 2. Experimental

### 2.1. Electrochemical cell

A three-electrode cell, consisting of a reference electrode, a Pt mesh counter electrode and a carbon steel working electrode, was used. In the case of all experiments conducted outside of the radiation environment, the reference electrode used was a saturated calomel electrode (SCE) (Fisher Scientific), whereas for radiation experiments a Hg/HgO reference electrode (Radiometer Analytical) in 1.0 M KOH solution was employed. The Hg/HgO electrode has been found to be more resistant to radiation than the saturated calomel electrode (SCE) or Ag/AgCl electrode, and has a potential of 0.112 V versus the standard hydrogen electrode (SHE). All potentials are quoted on the SCE scale (0.242 V vs. SHE). The working electrode in all experiments was A516 Gr70 carbon steel, purchased from Goodfellow (in wt.%: C, 0.20; Mn, 1.05; Si, 0.32; Al, 0.04; P, 0.015; S, 0.008; balance Fe). Prior to each experiment, the working electrode was polished manually with 600 and 1200 grit silicon carbide papers, followed by polishing on a Texmet microcloth (Buehler) with a 1  $\mu\text{m}$  MetaDi Supreme diamond paste suspension (Buehler), and lastly sonication in an acetone/methanol mixture for 5 min to remove polishing residues.

A Solartron model 1240 potentiostat and model 1252 frequency response analyzer were used in all electrochemical measurements. Corrware<sup>TM</sup> and Zplot<sup>TM</sup> software (Scribner and Associates) were used for experiment control and data analysis. EIS was performed by applying a  $\pm 10 \text{ mV}$  sinusoidal potential stimulus, either at the corrosion potential,  $E_{CORR}$ , or an applied potential,  $E_{APP}$ , while the analyzer converted the system response into an impedance value. The frequency was varied over the range  $10^4$  to  $10^{-2} \text{ Hz}$ . A second frequency scan consisting of measurements at several frequencies spanning the same range was then acquired to verify that the electrode surface remained at steady state over the course of the EIS measurement. Linear polarization measurements were performed by scanning the potential from the corrosion potential to  $-0.015 \text{ V}$  versus the corrosion potential, then to  $+0.015 \text{ V}$  versus the corrosion potential, and finally back to the corrosion potential, at a rate of  $0.1667 \text{ mV/s}$ .

### 2.2. Solutions

All experiments were conducted at room temperature in Ar-sparged 0.01 M sodium borate solutions. The solutions were pre-

pared using reagent grade  $Na_2B_3O_8$  (Caledon Laboratories Ltd.) and water purified using a NANOpure Diamond UV ultra-pure water system (Barnstead International), with a resistivity of  $18.2 \text{ M}\Omega \text{ cm}$ . Reagent grade NaOH (Caledon Laboratories Ltd.) was added dropwise to the solutions to adjust the pH. All experiments were conducted at a pH of 10.6.<sup>1</sup>  $H_2O_2$  was added from a 3 wt.% stock solution from Fisher Chemicals.

### 2.3. Irradiation source

All irradiation experiments were conducted in a MDS Nordion Gammacell 220 Excel Cobalt-60 irradiator. The electrochemical cell was positioned inside the gammacell sample chamber, and the chamber was lowered into the gammacell irradiation zone, consisting of 11 tubular pencils containing  $^{60}\text{Co}$ . The dose rate during the period of experimentation was  $\sim 6.8 \text{ kGy h}^{-1}$ .

### 2.4. Procedure

Following application of the polishing procedures described previously (Section 2.1), the working electrodes were rinsed with deionized water and placed in the electrochemical cell, which had been sparged with argon gas for at least 1 h to purge any oxygen from the solution. Electrochemical experiments then began with cathodic cleaning at  $-1.1 \text{ V}$  for 5 min to remove any residual air-formed oxides on the working electrode, thereby creating a virtually clean metal surface. The electrode was then anodized for 2.5 h at  $-0.7$ ,  $-0.2$ , or  $0.2 \text{ V}$  with the intention of generating a variety of oxide films with differing compositions and properties. When the potentiostatic film growth was completed, either, the electrochemical cell was irradiated in the gammacell for 6 h, or a specific concentration of  $H_2O_2$  was added to the solution;  $E_{CORR}$  was measured during the entire procedure.  $E_{CORR}$  monitoring continued for a number of hours (generally 24–48 h) to follow any changes occurring in solution and on the metal oxide surface.

Over the course of the experiments, periodic measurements of either EIS or LP were performed to aid in determining the change in the resistive nature of the oxide film. Also, to evaluate the radiolytic production of redox species, gaseous and aqueous samples were taken periodically for  $H_2O_2$  analysis by UV-vis spectrophotometry and for  $O_2$  and  $H_2$  analysis by gas chromatography.

In some cases, 24 h after the addition of  $H_2O_2$ , carbon steel samples were removed and analyzed using X-ray photoelectron spectroscopy (XPS).

### 2.5. Surface analytical instrumentation

The XPS data were acquired on a KRATOS Axis Ultra spectrometer using monochromatic Al  $K\alpha$  radiation and operating at 150 W, with a base pressure of  $10^{-8} \text{ Pa}$ . Under normal analysis conditions, the analysis spot size was approximately  $400 \mu\text{m} \times 700 \mu\text{m}$ . The energy scale of the instrument was calibrated with respect to C-1s (284 eV) [16–18]. Broad spectrum survey scans were recorded to verify surface composition and cleanliness, while high-resolution spectra, were used to examine certain bands of 3 elements in detail: Fe-2p (binding energy, BE, at 711 eV), O-1s (530 eV), and C-1s (284 eV).

<sup>1</sup> We are interested in pH 10.6 since the  $pH_a$  of the heat transport system coolant of a CANDU reactor is maintained between 10.2 and 10.4 to minimize corrosion of carbon steel and the deposition of corrosion products on fuel cladding surfaces, where  $pH_a$  is the pH meter reading obtained for a heavy water sample using pH electrodes calibrated with a light water buffer, all measured at  $25^\circ\text{C}$ .

Download English Version:

<https://daneshyari.com/en/article/190867>

Download Persian Version:

<https://daneshyari.com/article/190867>

[Daneshyari.com](https://daneshyari.com)