Western University – Clara Wren IRC

UNENE/NSERC IRC Program: Radiation-Induced Chemistry and Corrosion

Overview

This is the second progress report for the 3rd term of the NSERC IRC in Radiation-Induced Chemistry and Corrosion which was renewed in April 2016 by NWMO and UNENE. The aim of the research projects conducted in the 3rd term of the IRC is to provide the scientific and technical basis for: (1) assessment of the integrity and longevity of the weld design of the proposed NWMO Mark II container for long-term disposal of used nuclear fuel, and (2) assessment of the corrosion performance of CANDU nuclear reactor structural components, in particular, End Shield Cooling (ECS) systems. This report summarizes the progress against the IRC milestones for work addressing the concerns of UNENE.

As the nuclear power reactors are aging and their life-times are extended, accurate assessment of the integrity and longevity of the reactor structural materials is increasingly important. For example, current investigation into a leak in the End Shield Cooling (ESC) System in the Pickering Unit 6 nuclear reactor has raised a potential issue. Moisture from the ESC system leak could possibly reach a location in the annular air gap which exists around the periphery of the calandria tank assembly and its supporting structures where corrosion would be problematic and needs careful evaluation. In particular, the potential for accelerated (galvanic) corrosion attack on carbon steel (CS) adjacent to the dissimilar metal weld between CS (SA36) and stainless steel (SS) (SA240, Type 304L) at the periphery of the annular gap (**Fig. 1**) must be addressed.

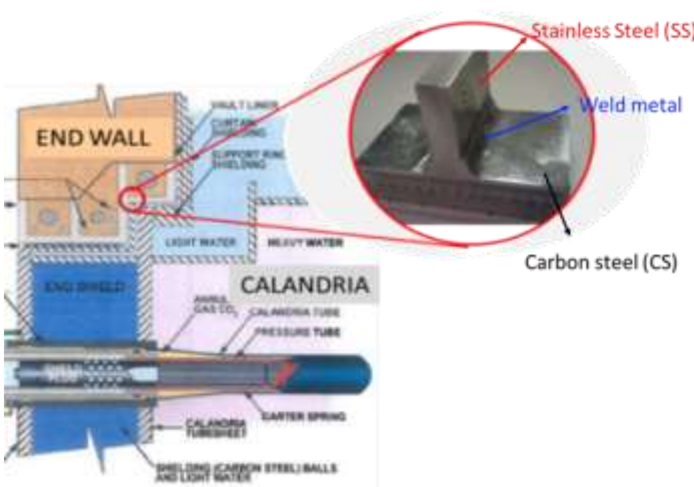

Fig. 1: Schematic of the calandria tank assembly and its supporting structures in a CANDU reactor. The red circle indicates the location of the carbon steel (CS) and stainless steel (SS) weld joint as shown in the inset circle.

Assessing the effects of water radiolysis on corrosion is difficult even in the absence of radiation. The difficult arises primarily because corrosion is already a complicated function of the chemical and physical properties of a solution in contact with metal, but the solution properties can change considerably as corrosion progresses. The rates of these changes depend on the concentration of redox active species present, pH and temperature. The annular gap environments include the added challenge of ionizing radiation that will drive radiolysis of liquid water. Radiolysis affects the redox conditions by decomposing water to create redox active species such as H_2O_2. The concentrations of these redox active species can effectively control the corrosion rates of metal alloys. Radiolysis of humid air also produces nitric oxides and nitric acid that are easily absorbed and lower the pH of any water in contact with the humid air. Since these radiolysis products can affect corrosion kinetics considerably, evaluating corrosion performance and the designs of chemistry control systems to limit corrosion in nuclear environments must consider the effect of radiation fields that are present, particularly γ-radiation, on water chemistry.

The scientific objective of the UNENE sponsored research is to determine the combined effects of γ-radiation and exposure environments (such as pH, temperature, ionic strength, dissolved O_2, [H_2O_2] and [HNO_3]) on corrosion of individual alloys (CS, SS and weld material (W = SS309) and galvanic corrosion at weld joints.

Progress in 2016-2017

Radiolysis Modeling of the Anticipated Annular Gap Environments

To determine radiolytically-produced oxidant concentrations that may be present and important to the steel (CS, SS and W) corrosion under the anticipated annular gap environments. two different radiolysis kinetic models are being developed: (1) water radiolysis and (2) humid air radiolysis. The kinetic models consider the primary radiolytic processes and chemical reactions of the radiolysis products. The progress to date includes: (1) construction of the models (i.e., assembling the key processes and their rate parameters (reaction orders and rate constants), (2) coding the rate equations for the concentrations of radiolysis products that are undergoing the coupled processes included in the models into a differential rate equation solver (commercial software FACSIMILIE), and (3) verification of the computer codes. The computer-coded models are being used to calculate the concentrations of radiolysis products as a function of exposure environmental parameters such as pH, temperature, dissolved O_2 and humidity. A study on the development of the humid air radiolysis model (HARM) and some calculation results has been published (see #1 in the publication list provided below). The calculations as a function of exposure parameters are continuing. Experiments to validate these models are being conducted to refine and identify the key reactions.

Effect of γ-Radiation on Independent Corrosion of Different Steels

The effect of γ-radiation on independent corrosion of the different steels (CS (SA36), SS (Type 304L) and weld metal (Type 309)) used in the end-shield tank supporting structures was studied by performing coupon exposure tests and electrochemical experiments in parallel. The steel coupons and electrodes were cut from samples supplied by Ontario Power Generation (OPG). The changes in the morphology and composition of the oxides formed on the steel surfaces were investigated using various surface imaging and spectroscopic analyses. The test solutions were analyzed for dissolved metal concentrations by using inductively coupled plasma – optical emission spectroscopy (ICP-OES). These studies help to develop a mechanistic understanding on the effect of γ-radiation on the corrosion of these steels when they corrode independently and to determine the effects of solution parameters coupled with γ-radiolysis on the corrosion pathways of these steels. These studies on independent corrosion provide a basis to assess the potential for accelerated (galvanic) corrosion attack on carbon steel (CS) adjacent to the metal weld.

The solution environments studied to date include different pHs (pH 6.0 and 10.6) and temperatures (25, 50 and 80 °C). These studies have shown that at a given pH and temperature SS Type 304L and Type 309 corrode at a slower rate than CS due to the presence of a preformed chromium oxide (Cr_2O_3) layer that hinders interfacial metal cation transfer, but the difference in corrosion rate between SS and CS diminishes with increasing pH (within the studied pH range). The better corrosion resistance at a higher pH for CS is attributed to the fact that dissolution of metal cations is quickly suppressed at the higher pH due to a lower solubility of metal cations, promoting earlier formation of a passive oxide layer. Gamma-radiation increases the overall corrosion rate for all three steels. However, the effect of γ-radiation on CS corrosion depends more on pH. In an acidic environment, metal dissolution is the major corrosion pathway and it is accelerated with radiation present. In a basic environment, CS corrosion is quickly suppressed by earlier formation of a protective oxide film. Some experimental results that show the improved corrosion performance of CS at pH 10.6 with or without radiation present are in Fig. 2.

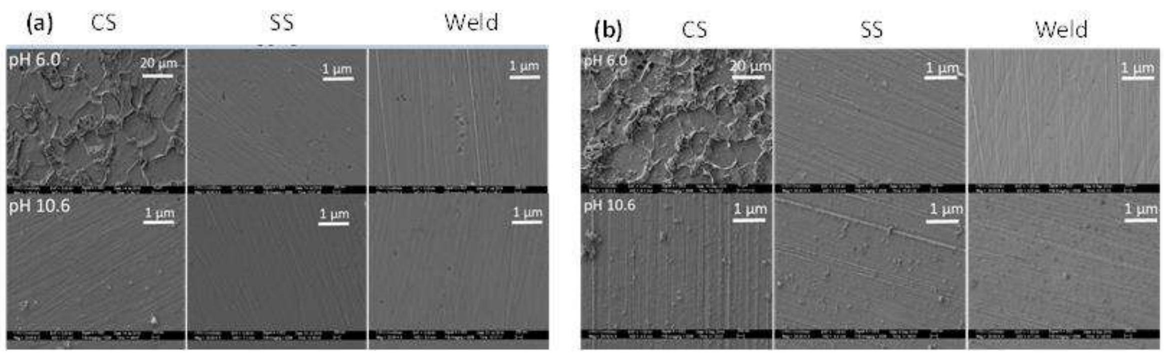

Fig. 2: SEM micrographs of CS, SS and Weld surfaces after corrosion for 72 h in pH 6.0 and 10.6 borate buffer solutions at 50 °C: (a) in the absence and (b) in the presence of radiation.

Radiolysis-induced galvanic corrosion of dissimilar metal welds

The galvanic corrosion of a CS-Weld couple was investigated by measuring the coupling potential and coupling current between a CS-Weld couple with and without radiation. The maximum oxidation rate of CS after galvanic coupling was found to be only about two times as high as the independent corrosion rate of CS with or without radiation. This was consistent with the solution analysis results, which shows that the dissolved Fe concentration measured after galvanic coupling is about 1.5 times higher that seen after independent CS corrosion. At a higher temperature (80 °C), the metal oxidation rate on CS was initially very high but the surface of the CS is quickly covered with a protective oxide layer, leading to the suppression of further metal oxidation on CS. In summary, these results indicate that galvanic corrosion of CS and Weld is not significant within the range of our studied experimental parameters.

A journal manuscript on the corrosion studies is in preparation.

Research Facilities And Equipment

The radiation assisted materials performance Science (RAMPS) laboratory led by the Chair is equipped with a suite of equipment for performing leading-edge research in the field of radiation-induced chemistry and corrosion. The major facilities and instruments in the laboratory include (**Fig. 3**):

- a Co-60 gamma radiation chamber that provides a high dose rate (2.2 kGy/h (May 2017)),
- a suite of electrochemical equipment including potentiostats and frequency response analyzers, ultra-low current and voltage measuring systems,
- several pressure vessels for high temperature/pressure water and supercritical water corrosion studies,
- a gas chromatograph with mass selective, thermal conductivity, electron capture detectors,
- a UV-Vis absorbance and fluorescence spectrometer, a photoemission spectrometer,
- an attenuated reflectance FTIR (Fourier transfer infrared) spectrometer,
- a scanning optical microscope with a very high resolution,
- an inductively coupled plasma-optical emission spectrometer (ICP-OES).

Fig. 3: Major equipment and instruments in the RAMPS laboratory.

In addition, the Chair's research team members have access to and receive training on a suite of sophisticated surface analysis instruments through Surface Science Western for SEM/EDX (scanning electron microscope/energy disperse x-ray), Auger, XPS (X-ray photoelectron spectrometer), profilometry, etc., the Biotron for TEM (transmission electron microscope) and ICP-MS (inductively coupled plasma – mass spectrometer), the Nanofabrication Facility (Nanofab) for Focus Ion Beam (FIB) and SEM/EDX, the Zircon and Accessory Phase Laboratory (ZAPLab) for EBSD (electron backscatter diffraction), and the Tandetron Accelerator Facility for heavy ion-beam irradiation.

HQP

Current (As of May 2017):

- 1.5 Research Associates: Dr. J. Joseph, Dr. G. Whitaker
- 9 PhD Candidates: M. Momeni, D. Guo, R. Morco, J. Turnbull, Y.G. Shin, M. Li, R. KarimHaghighi, M. Zakeri, M. Naghizadeh
- 4 MSc Candidates: C. Spark, M. Bahrami, L. Grandy, T.V. Do

Completed Training in 2016 – May 2017:

- Tom Sutherland, PhD
- Arielle Jean, MSc

Key Student Achievements and Honours in 2016 – May 2017:

- M. Li (2017): 1st prize, NACE Student Oral Presentation Competition
- Momeni (2017): Canadian Nuclear Society Jervis Student Achievement Award
- R. Morco (2017): Roy G. Post Foundation Scholarship (International)
- M. Zakeri (2016): Ontario Trillium Scholarship
- M. Li (2016): 1st prize, Annual UNENE Workshop Poster competition

Recognition

- Faculty of Science Graduate Student Mentoring Award (Sept 2016). Recognition for excellence in graduate student mentoring.
- Faculty of Science Distinguished Research Professorship Award (Jan 2015- Dec 2016), Provides the recipient with release from teaching and administrative duties in order to provide one year of full time research at Western.

Invited Talks (2016- May 2017)

- US DOE Workshop of Basic Research Needs for Future Nuclear Energy. Panel presentation, Rockville, Maryland, US, 2017.
- Radiolytic Corrosion of Copper. Peer Review of NWMO Copper Corrosion Program, Ottawa, ON, Canada, 2016.
- Research Activities on Radiation Assisted Materials Performance Science at Western University, Japan Atomic Energy Agency, Tokai-mura, Japan, 2016.
- Gamma-Radiolysis Induced Corrosion. Research Conference on Post-Accident Waste Management Safety (RCWM2016) and Safety Research for Radioactive Waste Storage, Iwaki City, Fukushima, Japan, 2016.

Publications (2016 – May 2017)

Summary: 10 papers in peer reviewed journals
9 conference proceedings – not listed
54 conference presentations – not listed

Peer-Review Journal Publications (Selected):

1. R. Morco, J.M. Joseph, D. Hall, C. Medri, D. Shoesmith, J.C. Wren*. Modelling of Radiolytic Production of HNO_3 Relevant to Corrosion of a Used Fuel Container in Deep Geologic Repository Environments. *Corr. Eng. Sci. Tech.*, 52, S1, 141-147 (2017).
2. T. Sutherland, C. Sparks, J.M. Joseph, Z. Wang, G. Whitaker, T-K. Sham, J.C. Wren*. Effect of Ferrous Ion Concentration on the Kinetics of Radiation-Induced Iron-Oxide Nanoparticle Formation and Growth. *Phys. Chem. Chem. Phys*., 19, 695-708, (2017).
3. Z. Wang, L. Alrehaily, J.M. Joseph, J.C. Wren*, J. Wang, T-K. Sham. Scanning Transmission X-ray Microscopy Studies of Chromium Hydroxide Hollow Spheres and Nanoparticles Formed by Gamma- Radiation. *Can. J. Chem*., Accepted (2017).
4. L. Wu, D. Guo, M. Li, J.M. Joseph, J.J. Noël, P. Keech, J.C. Wren*. Inverse Crevice Corrosion of Carbon Steel: Effect of Solution Volume to Surface Area. *J. Electrochem. Soc*., 164(9): C539-C553 (2017).
5. A.Y. Musa, J.C. Wren*. Combined Effect of Gamma-Radiation and pH on Corrosion of Ni-Cr-Fe Alloy Inconel 600. *Corros. Sci.,* 109 (2016) 1-12.
6. M. Momeni, M. Behazin, J.C. Wren*. Mass and Charge Balance (MCB) Model Simulations of Current, Oxide Growth and Dissolution in Corrosion of Co-Cr Alloy Stellite-6, *Journal of The Electrochemical Society*, 163 (3) C1-C12 (2016).
7. R.P. Morco, A.Y. Musa, M. Momeni, J.C. Wren*. Corrosion of Carbon Steel in the $[P_{14666}]$[Br] Ionic Liquid: The Effects of γ-Radiation and Cover Gas. *Corros. Sci.,* 102 (2016) 1-15.
8. V. Subramanian, J.M. Joseph, H. Subramanian, J.J. Noel, D.A. Guzonas, J.C. Wren*. Steady-State Radiolysis of Supercritical Water: Model Predictions and Validation. *ASME J. Nuclear Rad. Sci.,* 2016 (2016), 021021-1-021021-6.
9. Z.Y. Xin, Y.H. Ling, Y.K. Bai, C. Zeng, S. Wang, J.C. Wren*. Effect of Hydrogen Uptake on the Electrochemical Corrosion of N18 Zircaloy under Gamma-Radiation. *Appl. Surf. Sci*., 388: 252-258, (2016).
10. M. Sterniczuk, P. Yakabuskie, J.C. Wren, J. Jacob, D. Bartels. Radiolysis Escape Yields for Reducing Radicals and H_2 in Pressurized High Temperature Water. *Rad. Phys. Chem*., 121: 35-42, (2016).