A PROGRAM ON THE CORROSION OF CARBON STEEL IN THE PRESENCE OF WATER RADIOLYSIS

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ABSTRACT

Understanding the factors that can affect the corrosion of steel pipes or containers is important for material selection and effective operation and maintenance of nuclear power reactors. Corrosion kinetics depend on the aqueous redox condition and the physical and chemical nature of the steel surface involved. Nuclear plant environments include the added challenge of fields of ionizing radiation that can affect the redox conditions in solution. An NSERC/AECL Industrial Research Chair program has been established with the objective of developing a fundamental understanding of this synergistic interaction between the processes of radiolysis and corrosion. This presentation provides an overview of the research program and summarizes key findings.

1. INTRODUCTION

The chemical effects of radiation on materials degradation are a major uncertainty in the nuclear industry. Ionizing radiation (e.g., neutron, α, β, γ-radiation) decomposes water to yield a range of chemically reactive products [1,2]:

$$H_2O \quad \rightarrow \quad \bullet OH,\ \bullet e_{aq}^{-},\ H\bullet,\ HO_2\bullet,\ H_2,\ H_2O_2,\ H^{+} \qquad (1)$$

In a constant radiation field, these radiolysis products achieve low but steady-state levels. These steady-state concentrations dictate the aqueous redox condition that controls corrosion reactions, but can be easily affected by reaction with dissolved species. For example, corrosion of metals introduces dissolved impurities, such as Fe^{2+}/Fe^{3+}, which can, in turn, catalytically interact with radiolytic decomposition products of water. The net effect of this synergistic interaction on metal corrosion and corrosion product transport is often difficult to predict. Despite their importance, these synergistic interactions between water radiolysis and material degradation, Figure 1, are not well understood.

An Industrial Research Chair (IRC) program in Radiation Induced Processes, funded by the Canadian Natural Science and Engineering Research Council (NSERC) and Atomic Energy of Canada Limited (AECL), has been established to develop a fundamental understanding of the effects of water radiolysis on system chemistry and materials degradation in nuclear reactor environments, with a particular focus on the chemical effects of ionizing radiation. The research projects established under this program include:

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(1) Catalytic effects of dissolved chemical additives (corrosion products and pH- or redox-controlling agents) on water radiolysis
(2) Steel corrosion in aggressive redox environments that simulate radiolytic environments
(3) Steel corrosion in a gamma-irradiation field

A combination of chemical, electrochemical and surface analytical techniques is used in these studies. Computational model analysis is also used to interpret the experimental data and to develop a predictive capability. The chemical reaction and transport rate equations for the complex interfacial systems are solved using the commercial software codes, FACSIMILE and COMSOL-Multiphysics. This paper provides an overview of the research program and summarizes key findings to date.

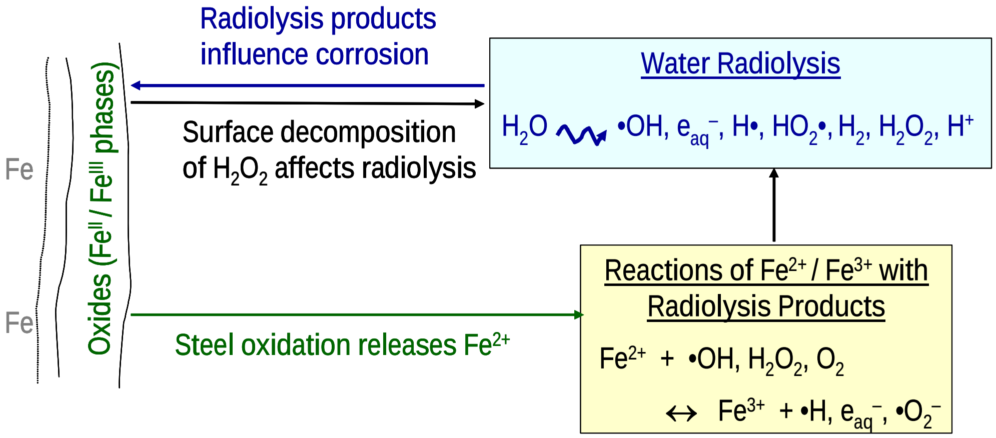

Figure 1: Schematic representation of synergistic interactions between water radiolysis and steel corrosion.

2. RESULTS AND DISCUSSION

2.1 Catalytic effects of dissolved chemical additives on water radiolysis

The radiolytic decomposition of water produces both oxidizing ($\bullet OH$, O_2, H_2O_2, etc) and reducing species ($\bullet H$, $\bullet e_{aq}^-$, $\bullet O_2^-$, etc), affecting the redox chemistry that controls corrosion. Corrosion reactions are surface reactions with relatively large activation energy and, hence, occur on considerably longer time scales. Consequently, the steady-state concentrations of water radiolysis products, not the primary yields (G-values) determined within less than 100 ns following absorption of radiation energy, are important for corrosion kinetics. While dissolved species at impurity levels do not significantly affect the primary yields, they can significantly alter the steady-state concentrations.

The dissolved species that are being studied under the IRC fall into three categories:

(1) *Molecular redox products*, H_2, O_2 and H_2O_2 are of primary interest, since their effect on water radiolysis behaviour depends on their relative concentrations. For example, small excess concentrations of H_2 (added during start-up in some CANDU reactors) can significantly suppress the net radiolytic breakdown of water by scavenging the initially-formed free radicals (e.g., •OH). By contrast, similar concentrations of H_2 produced with stoichiometric quanitites of O_2 (and H_2O_2) cannot suppress radiolysis and its concentration can achieve a high value over long irradiation times. From the corrosion perspective, molecular radiolysis products, due to their much higher steady state concentrations, are considered to be more important than radical products.

(2) *Soluble corrosion products* from most reactor piping are transition metal ions (iron, manganese, chromium, nickel ions, etc). They can easily form redox pairs at ambient electrochemical potentials such that, even at small concentrations, they can catalytically interact with radiolysis products. A program goal is to establish a quantitative relationship between the steady-state concentrations of radiolysis products (radicals vs. molecules) and the equilibrium potential of a redox couple. The solubility of a metal ion is a very sensitive function of its oxidation state and pH, and the conversion between two oxidation states by radiolysis may influence the solubility of metallic species and can be an important parameter for corrosion product transport in piping.

(3) *Nitrogen containing compounds*, such as ammonia, nitrate and hydrazine, can enter the reactor coolant via air ingress (air radiolysis) or the decomposition of ion exchange resins. Air radiolysis can also affect radioiodine volatility and radiolytic H_2 production in containment buildings in the unlikely event of an accident, and nitric acid is used in nuclear waste treatment and fuel processing, and ammonia or hydrazine are used for in-reactor pH and corrosion control. The interaction of these compounds with water decomposition products is complex since a wide range of oxidation states exist for nitrogen.

The effects of the dissolved species on the radiolysis kinetics and steady-state behaviour are being studied a function of pH, concentration of dissolved species, temperature and aqueous-gas interfacial partitioning in a ^{60}Co γ-irradiation cell (2.5 $Gy{\cdot}s^{-1}$ on Sept 2007)). Radiolysis kinetics are followed by measuring the concentrations of radiolytic H_2, O_2, H_2O_2 and the aqueous reactants and products, e.g., Fe^{2+} and Fe^{3+} and NO_3^- and NO_2^-, as a function of either time or total absorbed dose. Chemical kinetic and mass transport models are under development using the FACSIMILE and COMSOL Multiphysics codes. These studies provide the mechanistic understanding and databases for extrapolating to conditions inaccessible experimentally or where only integrated measurements are feasible. Studies at temperatures up to 150°C are underway, with plans to extend investigations to 350°C.

Preliminary room temperature findings include the following [2].

1. While the main path for H_2O_2 and H_2 production is the primary radiolytic decomposition of water, H_2O_2 removal occurs by reaction with $•e_{aq}^-$ and •OH, and for H_2 by reaction with •OH. As a result, the presence of a dissolved species, or a change in chemical environment, affects the concentrations of H_2O_2 and H_2 primarily through interaction with these radicals (Figure

2). From the perspective of water chemistry control by chemical additives, their reactivities with water radiolysis radicals are important considerations.

2. Over a wide range of the type and concentration of dissolved species and experimental conditions, there exist semi-quantitative but simple relationships between the radical and the molecular product concentrations. Molecular species are easier to monitor, and this study shows that radical behaviour can be inferred from that of the more easily measurable molecular species.

3. The steady-state concentrations of water decomposition products are effectively independent of pH in the range 5 – 8 (Figure 2). However, raising the pH above the pKa for the acid-base equilibrium of •H ($\leftrightarrows$ •e_{aq}^- + H^+) significantly increases [H_2O_2] and [H_2] at the expenses of [•OH] and [•e_{aq}^-]. Such a pH dependence is not expected based on the primary radiolysis yields. From the perspective of chemistry control for corrosion under irradiation conditions, pH may influence corrosion not only via its effect on equilibrium potentials for metal oxidation/reduction and the solubility of metal species, but also via its effect on the radiolytic production of aqueous redox species such as H_2O_2. In particular, a small change in pH around 9 may induce a significant change in aqueous redox conditions that would not be expected under non-irradiated conditions.

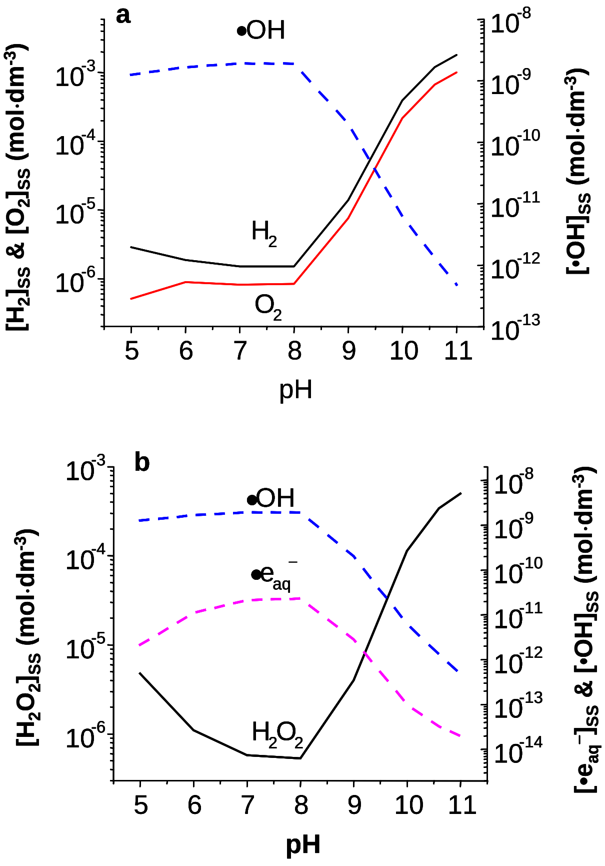

Figure 2: Steady-state concentrations of (a) H_2 vs •OH; (b) H_2O_2 vs •OH and •e_{aq}^- as a function of pH under de-aerated conditions at a dose rate of 2.5 kGy/s

4. Since molecular and radical product concentrations are inversely related, their steady-state concentrations have approximately square root dependencies on dose rate over a wide range of dose rates, Figure 3. These quantitative relationships allow the comparison of experimental data obtained under different dose rate conditions.

5. Dissolved species, including OH^-, O_2, metallic ions and nitrate, increase [H_2O_2] and [H_2] while decreasing [•OH] and [•e_{aq}^-]. This may have significant implications for corrosion

control, since the molecular species are more effective redox species for surface reactions than radical species. On the other hand, it is the reactions with radical species in the aqueous phase that determine the radiolytic production of volatile species such as iodine and hydrogen.

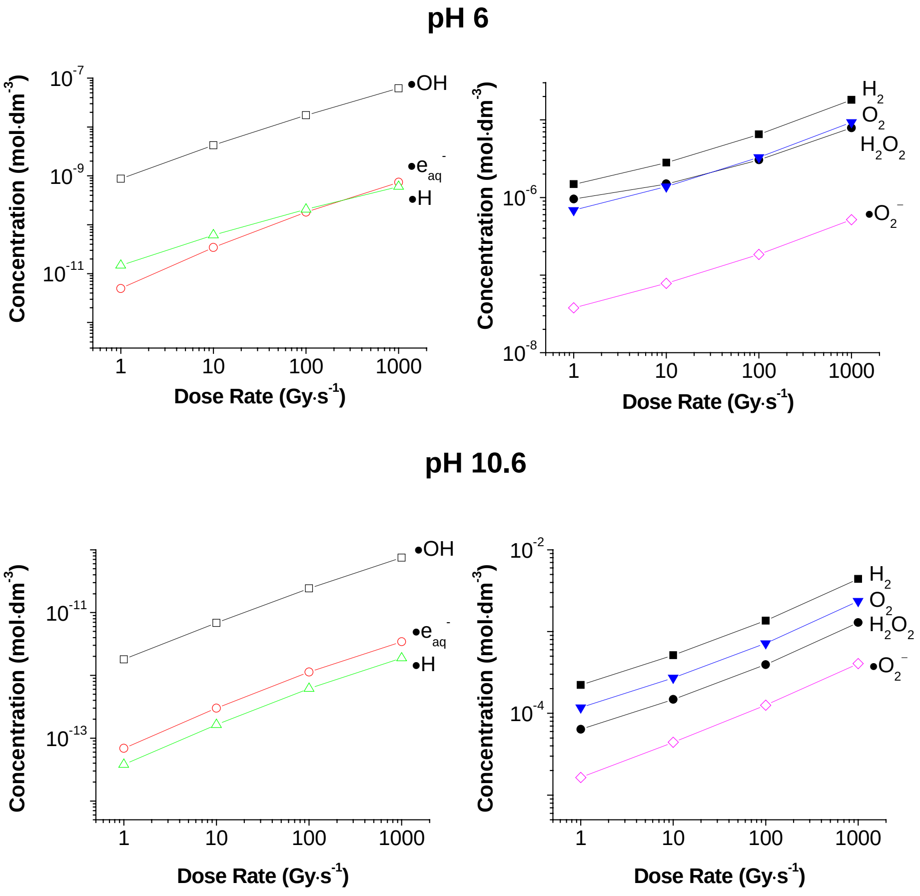

Figure 3: Steady-state concentrations of radical and molecular water decomposition products as a function of does rate at pH 6 and 10.6 under de-aerated conditions

2.2 Corrosion in aggressive redox environments

The nature and morphology of the surface oxide is an important parameter in controlling the corrosion rate of metal. Although carbon steel corrosion has been studied extensively, the mechanisms of oxide film formation and conversion are still not definitely established, making comparison of the studies performed under different conditions difficult. Most studies have been performed in either very basic solutions (pH > 13) or borate buffer solutions at pH 8.4, while the pHa[1] of the heat transport system coolant of a CANDU reactor is maintained between 10.2 and 10.4 to minimize flow accelerated corrosion of carbon steel and to minimize the deposition of

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[1] pHa is the pH meter reading obtained for a heavy water sample using pH electrodes calibrated with a light water buffer, all measured at 25°C.

corrosion products on fuel cladding surfaces. Systematic studies on oxide film formation/ conversion as a function of aqueous redox condition at this pH are rare. Corrosion rate measurements at this pH have generally been limited to the low corrosion potentials (E_{CORR}) expected in pure water systems, whereas water radiolysis generates a more oxidizing environment that would change E_{CORR}. Thus, the kinetics of film formation and conversion on carbon steel are being studied in detail, with the following studies presently underway.

(1) *Oxide film formation and conversion on carbon steel* to establish the stability of passive oxides under the dynamic redox conditions expected in the presence of radiation. Passivity is being studied by anodically growing films at different electrochemical potentials, studying their behaviour by varying the potential in different ways while monitoring the current response. The carbon steel electrode surfaces at various stages of film formation and conversion are subsequently analyzed using Electrochemical Impedance Spectroscopy (EIS) and other surface analysis techniques such as SEM/EDX (Scanning Electron Micrography/Energy Disperse X-Ray spectroscopy), Raman Spectroscopy/Confocal Raman Microscopy, XPS (X-ray Photoelectron Spectroscopy), XRD (X-Ray Diffraction) and Auger spectroscopy. The effects of pH, film growth potential, temperature, and convective conditions are being examined.

(2) *Film breakdown/conversion processes in the presence of halides*, to locate the potentials at which breakdown/conversion processes occur. These processes would otherwise be difficult to observe since in the absence of halides the film would be quickly repaired. While these ions themselves are not an in-reactor issue they help to locate subtle conversion/breakdown processes in the films. For this purpose, experiments similar to those used in the first study are performed, but with halides present either from the beginning or added at later stages of an experiment.

(3) *Interactions of molecular radiolysis products (H_2, O_2 and H_2O_2)* with anodically grown oxide or oxy/hydroxide films on carbon steel as well as with chemically grown single-phase films. This study is described together with the study on steel corrosion in γ-irradiation environments in the next section.

Studies are presently being carried out at room temperature to develop mechanistic and quantitative understanding and, eventually, a corrosion kinetic model with a predictive capability under dynamic aqueous redox conditions. Some results are presented in Figures 4 and 5. Studies as a function of temperature, for $T < 150^{o}C$, are now underway, and the design, preparation and testing of various components for electrochemical studies at temperatures greater than 250°C have started.

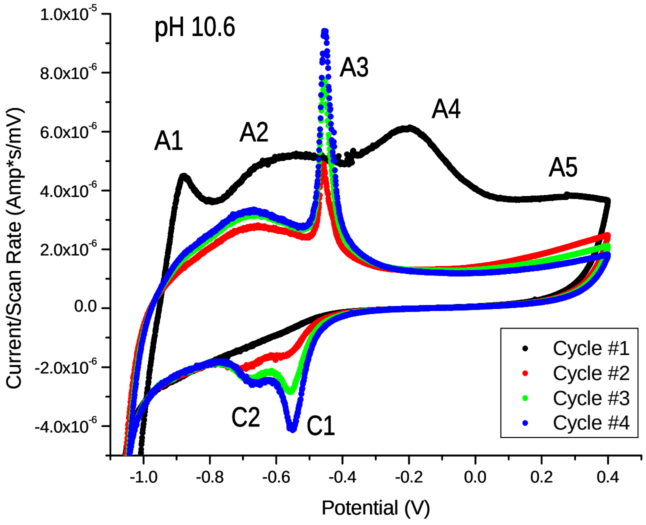

Figure 4:

Cyclic Voltammograms recorded on carbon steel as a function of scan cycle number at pH 10.6 and a scan rate of 5 mV/s;

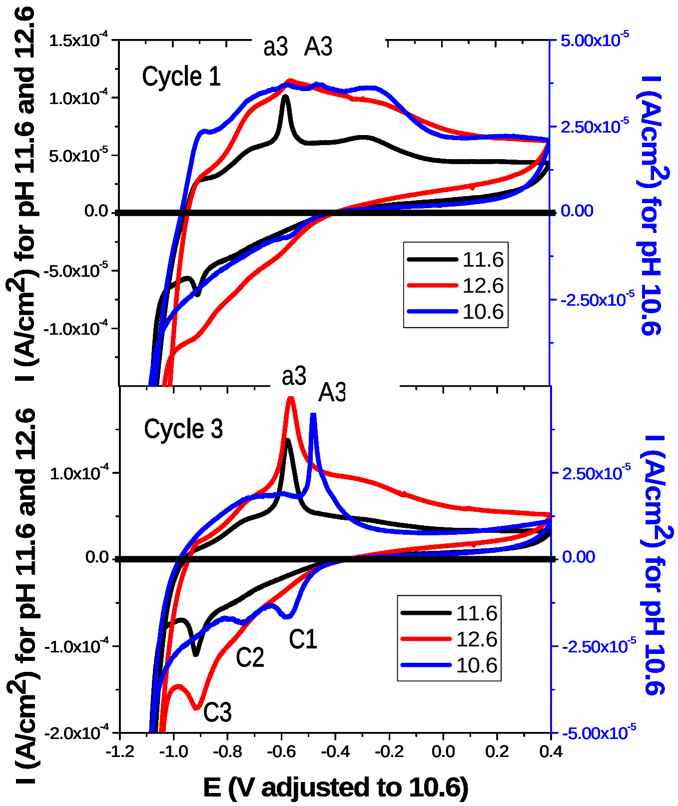

Figure 5:

Cyclic voltammograms as a function of pH during the first cycle (top) and the third cycle (bottom) at a scan rate of 5 mV/s. The potentials for the CVs obtained at pH 11.6 and 12.6 were shifted by 0.059 and 0.118 V to compare with the CVs taken at pH 10.6. Note that the current scale for pH 10.6 is shown on the right hand side, different from that for pH 11.6 and 12.6 on the left hand side.

Preliminary conclusions from these studies at room temperature are as follows [3,4].

1. The electrochemical and surface analytical studies on oxide film formation and conversion yield a consistent picture of film formation/conversion processes on carbon steel, and show that the behaviour under mildly basic conditions, pH 10.6, is different to that reported for basic (pH > 13) or near neutral solutions (pH < 8.4). Based on cyclic voltammetric and constant potential experiments, three distinct potential regions can be defined at pH 10.6 and room temperature.

2. Oxide film formation/conversion mechanisms for three potential regions were proposed for room temperature and pH 10.6:
   - In region I (≤ -0.6 V vs SCE), the main oxide formed is Fe_3O_4 which grows via a solid state process, although in the very early stages of film formation highly soluble Fe^{II} oxides/hydroxides are formed;
   - In region II ($-0.5V \leq E$ (vs SCE) ≤ -0.2 V), continuous growth of the Fe_3O_4 layer is accompanied by its anodic conversion to a more maghemite (γ-Fe_2O_3)-like phase near, or at, the oxide/solution interface by a similar solid-state mechanism;
   - In region III (0.0 V $< E$ (vs SCE) < 0.4 V), the anodic conversion of this Fe_3O_4/γ-Fe_2O_3 oxide to γ-FeOOH leads to significant structural changes, which can induce film fracture and the introduction of enhanced transport pathways in the film.

3. The potential implications for corrosion of these film formation processes at pH 10.6 can be summarized as follows:
   - Region I (≤ -0.6 V vs SCE) is a redox active region, in which soluble Fe^{II} oxides form. Although the formation of a less soluble magnetite film somewhat reduces iron dissolution, iron dissolution can be potentially high;
   - The lower potential end of Region II (-0.5 V $\leq E$ (vs SCE) ≤ -0.2 V) is also redox active, as seen by the high current for peak A3 in Figure 4. However, the redox reaction involves the conversion of conducting, but insoluble magnetite to insulating and insoluble maghemite, which induces passivity and prevents iron dissolution. It appears that the coversion is kinetically facile and near reversible since it does not induce significant oxide structural changes in the film.
   - The current observed in Region III (0.0 V $< E$ (vs SCE) < 0.4 V) is relatively small in the absence of aggressive anions, Figure 4. However, this is the potential region where a significant film phase change can lead to localized corrosion under appropriate aqueous chemical conditions.

4. Studies of the film formation and conversion processes in the presence of halides shows that, irrespective of halide concentration and type, breakdown never occurs below a critical potential of 0 V vs SCE, suggesting the key feature leading to breakdown is the subtle changes in oxide structure/composition which occur at higher potentials. One possible interpretation is that the electric field assisted conversion of the Fe_3O_4/γ-Fe_2O_3 oxide to γ-FeOOH, which becomes thermodynamically possible in this potential range, leads to a volume change that creates stress in the oxide film, eventually causing film fracture. In halide free solutions these defects in the oxide film can be rapidly repaired by further

Fe_3O_4/γ-Fe_2O_3/γ-FeOOH growth. However, in the presence of halide ions, halide transport to the metal/oxide interface prevents repassivation, leading to pit initiation.

5. Since the formation and conversion of $Fe^{II/III}$ and Fe^{III} oxides on carbon steel are kinetically facile processes, anodic oxidation of iron requires little overpotential and corrosion potentials would be expected to be located close to equilibrium potentials.

6. The extent of oxidation, or the average valence of Fe in the oxide layer, is determined by the film growth potential (or corrosion potential under naturally corroding conditions), while the film thickness at steady state is related to the potential and solubilities of the oxides formed. Thus, any change in thermodynamic conditions, for example due to radiolytic production of aqueous redox species or pH, then becomes very important in determining the corrosion rate.

2.3 Corrosion in a Gamma-Irradiation Field

The effect of γ-radiation on carbon steel corrosion is being investigated and compared to that of chemically added H_2O_2 and dissolved O_2.

Various oxide films are grown potentiostatically on carbon steel electrodes, and then exposed to γ-radiation at a dose rate of ~2.5 Gy/s. The corrosion kinetics are followed by monitoring the corrosion potential, E_{CORR}, and periodically performing linear polarization (LP) and EIS measurements. The concentrations of radiolysis products, H_2O_2, O_2, and H_2, were measured as a function of irradiation time by Gas-Chromatography and UV-Vis spectrometry. A water radiolysis model, which consistently and accurately predicted the measured concentrations of molecular redox species, was used to aid interpretation of the behaviour of unstable radical redox species ($\bullet O_2^-$, •OH), and to interpret the electrochemically-observed corrosion behaviour of the steel. Based on this understanding of the influence of radiolysis products, detailed corrosion kinetic measurements are also performed on oxide-covered carbon steel surfaces exposed to H_2O_2, which is believed to be the key radiolytically produced redox species at room temperature. The composition and morphology of surface oxides, in turn, have a significant influence on H_2O_2 decomposition. Thus, the surface oxidation and reduction of H_2O_2 is also being investigated on single phase iron oxide/hydroxide films. These electrochemical studies are augmented by various surface analyses as listed above. These studies, at temperatures up to 90°C, are well underway, and will soon be extended to higher temperatures.

Preliminary conclusions from these studies are as follows [5].

1. E_{CORR} values reached during and after γ-irradiation are reasonably well reproduced in experiments in which H_2O_2 is added to reach the concentration level achieved at the end of irradiation, Figure 6. The continuous addition of H_2O_2, rather than a single addition, yields the E_{CORR} changes which more closely mimic those observed during irradiation in which $[H_2O_2]$ increases with irradiation time, supporting the claim that the key radiolytic redox product is H_2O_2.

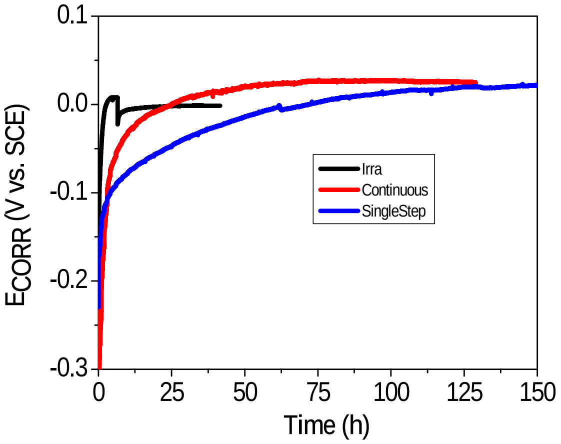

Figure 6: The effect of gamma-radiolysis and chemically added H_2O_2 on E_{CORR} recorded on carbon steel anodically oxidized at different potentials. The final $[H_2O_2]$ was 10^{-4} M, whether added in an initial single injection or in continuous addition.

2. The interaction of H_2O_2 with the oxide films was further examined over a wide range of $[H_2O_2]$, Figure 7. At high $[H_2O_2]$, E_{CORR} rapidly reached a steady-state value of 0.05 V, independent of both the type of oxide film initially grown and $[H_2O_2]$. This potential value is between the equilibrium potentials for H_2O_2 reduction to OH^- and H_2O_2 oxidation to O_2. This suggests E_{CORR} at high $[H_2O_2]$ is controlled by the surface decomposition of H_2O_2. At lower concentrations, H_2O_2 acts as either a reductant or oxidant depending on the nature of the oxide.
3. Linear polarization and EIS measurements as a function of either irradiation time or time after addition of H_2O_2 are in progress. Results obtained to date also show similar trends for the irradiated and the chemically-added H_2O_2 systems.

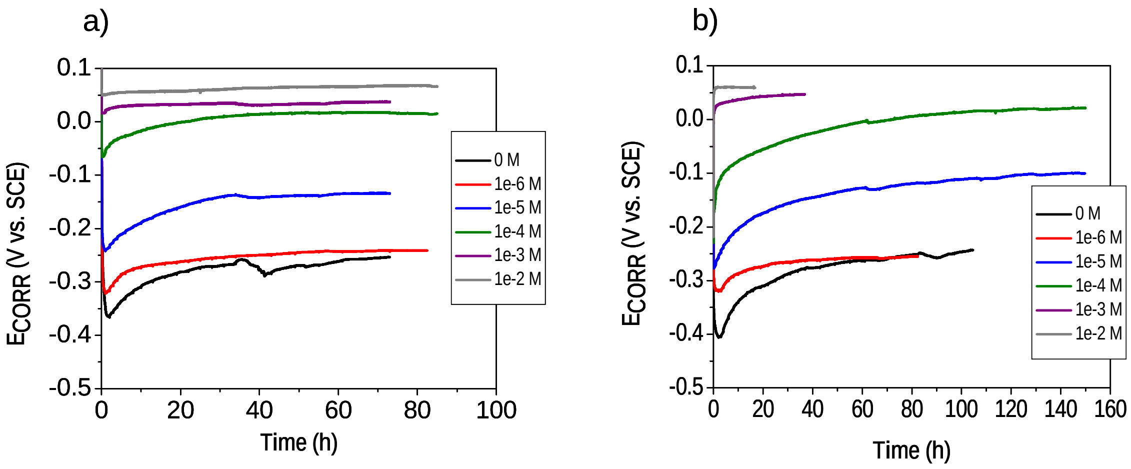

Figure 7: E_{CORR} during exposure to H_2O_2 for carbon steel with oxide films potentiostatically grown at (a) 0.2 V (vs. SCE) and (b) –0.2 V vs. SCE. $[H_2O_2]$ ranged from 0 to 1×10^{-2} M. H_2O_2 was added at time = 0 h.

3. SUMMARY

The aqueous redox condition strongly influences the steel corrosion mechanism and kinetics. Ionizing radiation can significantly affect the redox conditions in solution. Even under nominally steady-state radiolysis conditions, the solution redox conditions may change considerably as corrosion progresses since soluble corrosion products can react synergistically with the water radiolysis products. A comprehensive research program has been established to develop a fundamental understanding of these synergistic interactions between radiolysis and corrosion. The progress and preliminary conclusions from the program have been summarized.

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