APPLICATION OF A
PASSIVE ELECTROCHEMICAL NOISE TECHNIQUE
TO LOCALIZED CORROSION OF
CANDIDATE RADIOACTIVE WASTE CONTAINER MATERIALS

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ABSTRACT

One of the key engineered barriers in the design of the proposed Yucca Mountain repository is the waste canister that encapsulates the spent fuel elements. Current candidate metals for the canisters to be emplaced at Yucca Mountain include cast iron, carbon steel, Inconel 825 and titanium code-12. This project was designed to evaluate passive electrochemical noise techniques for measuring pitting and corrosion characteristics of candidate materials under prototypical repository conditions. Experimental techniques were also developed and optimized for measurements in a radiation environment. These techniques provide a new method for understanding material response to environmental effects (i.e., gamma radiation, temperature, solution chemistry) through the measurement of electrochemical noise generated during the corrosion of the metal surface. In addition, because of the passive nature of the measurement, the technique could offer a means of in-situ monitoring of barrier performance.

Testing was completed to compare the effects of temperature, radiation and simulated radiation using hydrogen peroxide. For tests using Inconel counter electrodes and carbon steel working electrodes at 25, 50 and 90°C, the increased temperature produced a higher mean voltage as expected. The 90°C run also had a large increase in standard deviation compared to the lower temperature runs.

For data analysis, the power spectral density (psd) of the entire current trace for each run was calculated in decibels within the frequency range of interest. Analysis of the psd was interpreted to indicate localized corrosion in the low frequency range and general corrosion in the higher frequency range.
For the temperature comparison runs, an increased temperature produced higher corrosion activity along the entire frequency range.

To compare the effects of radiation, tests were done with titanium counter and working electrodes at 90°C using the MITRII spent fuel pool for the radiation source. The radiation environment caused the mean current value to be much lower, and the psd curve also showed less activity for the run exposed to radiation. To simulate radiation, one ppm hydrogen peroxide was added to some tests with carbon steel as the working and counter electrodes. This had no significant effect on either the current trace or the psd. One ppm hydrogen peroxide was determined to be insufficient to replicate the chemical changes produced by irradiation of the magnitude expected at the proposed Yucca Mountain repository.

Increased temperature has been shown to increase the localized corrosion of active metals such as carbon steel, and substantial radiation decreased the localized corrosion activity of stable metals such as titanium. The pitting factor and total corroded volume are very useful parameters for providing further understanding and verification of the electrochemical noise data. However, the errors in the corrosion analysis procedure need to be reduced before this information can be used as more than an order of magnitude approximation.

Further work is needed to provide a more fundamental understanding of the results which have been obtained. A larger number of test runs is necessary to decrease statistical errors and verify these results. With the use of fiber optics for in-situ monitoring of the chemistry at the surface of the electrodes, more information can be obtained about the mechanisms involved. Changes in pH at the electrode surface during the onset of pitting can be determined as can concentrations of hydrogen peroxide and other species.
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1 Background

Permanent disposal of high level nuclear waste is an unresolved issue in the United States. The waste, mainly spent fuel from nuclear power plants and liquid waste from defense reprocessing operations, is currently stored at power plants or in large tanks at defense facilities. However, these sites are only a temporary solution until a final resting place is available. The current plan in the United States is to store the spent fuel in metal containers within a deep geological mined cavity. Liquid waste from defense operations will be solidified in glass and stored in the same mined cavity. All these wastes will need a primary release barrier, the canister, which is the subject of this thesis.

High temperature and radiation effects associated with high level nuclear waste, specifically spent fuel, are discussed in Section 1.1. Section 1.2 describes high level nuclear waste canisters including the current design and the metals under consideration. General corrosion of the canisters and non-uniform corrosion as pitting is discussed in Section 1.3. Section 1.3 also provides information on previous applications of electrochemical analysis. The purpose and goals of this project are noted in Section 1.4.

1.1 High Level Waste

The currently proposed design for the geological repository at Yucca Mountain would dispose of spent fuel from both boiling water reactors (BWR) and pressurized water reactors (PWR) in metal canisters. These spent fuel elements are sources of intense radiation and heat since they contain an assortment of fission products and actinides created during reactor operation. Beta and gamma rays contribute most of the heat through energy deposition in the fuel and immediate surroundings, while only gamma rays are a factor in dose outside the canister. Fission products dominate the radioactivity and decay heat for the first 150 years after discharge from the reactor, and then the actinides become relatively more significant. Table 1.1 lists the decay power and activity at discharge of the significant fission products and actinides for a 1000 MWₑ PWR with 33 MWD/kg burnup. Radionuclides that decay in the first ten years after discharge or have half-lives greater than 100,000 years (except for Tc-99, I-129 and U-234) are excluded.¹

Table 1.1. Decay Power from Fission Products and Actinides

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Half-life yr</th>
<th>Activity Ci/yr</th>
<th>Decay Power W/yr</th>
<th>Decay Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>*H-3</td>
<td>12.4</td>
<td>1.9E4</td>
<td>0.64</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>*Kr-85</td>
<td>10.8</td>
<td>3.1E5</td>
<td>503</td>
<td>$\beta^-$</td>
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<tr>
<td>Sr-90</td>
<td>27.7</td>
<td>2.1E6</td>
<td>2751</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>Nb-93m</td>
<td>13.6</td>
<td>3.95</td>
<td>0.04</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>Tc-99</td>
<td>2.1E6</td>
<td>390</td>
<td>0.26</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>Cd-113m</td>
<td>13.6</td>
<td>286</td>
<td>0.38</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>Sb-125</td>
<td>2.71</td>
<td>2.4E5</td>
<td>798</td>
<td>$\beta^-, \gamma$</td>
</tr>
<tr>
<td>*I-129</td>
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<td>1.01</td>
<td>0.001</td>
<td>$\beta^-$</td>
</tr>
<tr>
<td>Cs-134</td>
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<td>7.1E4</td>
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</tr>
<tr>
<td>Cs-137</td>
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<tr>
<td>Pm-147</td>
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<td>2.8E6</td>
<td>1444</td>
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<td>Sm-151</td>
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<td>3.4E4</td>
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<td>$\beta^-$</td>
</tr>
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<td>Eu-152</td>
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<td>341</td>
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<td>$\beta^-, \text{EC}$</td>
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<td>19.4</td>
<td>0.56</td>
<td>$\alpha$</td>
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<td>4.66</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Pu-238</td>
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<td>1.0E5</td>
<td>3314</td>
<td>$\alpha$</td>
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<tr>
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<td>$\alpha$</td>
</tr>
<tr>
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<td>405</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Pu-241</td>
<td>13.2</td>
<td>2.8E6</td>
<td>116</td>
<td>$\alpha, \beta^-$</td>
</tr>
<tr>
<td>Am-241</td>
<td>458</td>
<td>4.5E3</td>
<td>150</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Am-242m</td>
<td>152</td>
<td>116</td>
<td>0.05</td>
<td>$\alpha, \text{IT}$</td>
</tr>
<tr>
<td>Am-243</td>
<td>7950</td>
<td>477</td>
<td>15.4</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Cm-243</td>
<td>32</td>
<td>90.3</td>
<td>3.29</td>
<td>$\alpha, \text{EC}$</td>
</tr>
<tr>
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<td>7.4E4</td>
<td>2589</td>
<td>$\alpha$</td>
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<tr>
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<td>9300</td>
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<td>0.33</td>
<td>$\alpha$</td>
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<tr>
<td>Cm-246</td>
<td>5500</td>
<td>1.9</td>
<td>0.06</td>
<td>$\alpha$</td>
</tr>
</tbody>
</table>

* volatile fission product
1.1.1 Temperature

After the first 150 years in the repository, most of the fission product decay heat contribution is gone. Long-lived actinides are still producing significant heat though, mainly Am-241 and several of the plutonium isotopes. Even though only a small fraction of the initial decay power remains, this heat must be considered in repository loading considerations and spent fuel storage unit designs. Spent fuel entering the repository is expected to have a thermal output of 1.3 to 3.3 kW per container. The temperature histories of the waste packages are a function of the thermal properties of the near-field rock, specific configuration of repository boreholes and emplacement drifts, heat transfer mode and container output power.

Assessments of these parameters for a hot repository predict that the temperature at the container wall will remain above 100°C for at least 300 years after placing the package in the repository.\(^2\) Since the temperatures are predicted to be above the boiling point, liquid water would also be predicted to be excluded from the near-field repository environment for several hundred years; however, water may be present in rock pores as a liquid up to 140°C.\(^3\)

One consequence of the elevated temperature in the repository will be boiling of the groundwater in the host rock near the waste package, resulting in changes in the concentrations of silicon, aluminum, magnesium, calcium, etc. Figure 1.1 shows the drying zones around the waste package from waste heat. Water vapor from boiling does not readily move in the matrix. If there is a fracture nearby, the vapor moves to the fracture, where it is forced away from the waste package by higher gas pressure in the boiling zone caused by vapor production. Heat-pipe effects may occur and keep the area around the waste package near the boiling isotherm because of two-phase refluxing in the fractures. Vapor may also be driven outward through fractures and refluxing to the waste package could then occur in the matrix.

Waste packages may also be contacted by water during times of episodic liquid water movement through the repository. The possibility of episodic fracture flow has been recognized for several reasons: precipitation depends

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strongly on surface topography rather than falling uniformly, subsurface infiltration is higher in high-permeability pathways such as fractures, and precipitation is infrequent but occurs in short intense thunderstorms. Episodic fracture flow has important implications for aqueous transport. In fracture-dominated flow, the concentration field of a species depends on the geometric properties of the fracture network. Sorption onto fracture surfaces retards the movement of species under fracture-dominated flow. As a result, the geochemistry of water reaching the waste packages through episodic events will be different from water extracted in the matrix.4

Figure 1.1. Groundwater Behavior Near Waste Package

1.1.2 Radiation Effects

After the first 150 years, some of the radionuclides still have a relatively high activity. The effects of this long-term, low dose rate irradiation in combination with the high temperature and aggressive chemical environment on the waste canister must be carefully considered to ensure that the barrier is not breached before at least 300 years.

The influence of a radiation field on a repository has received relatively little attention, although the research done on the effects for water and dilute aqueous systems is much more extensive. The highest levels of radiation are present when the waste is emplaced, after which the radiation levels continue to decay. The radiation of most interest concerning container corrosion effects is gamma radiation, but fortunately most fission products resulting in gamma decay have relatively short half-lives. The long-lived actinides are predominantly alpha emitters, so their radioactive contribution is unimportant for container performance. Since alpha and beta particles cannot penetrate the primary barrier while it is still intact, these particles are not of major concern until the waste container is breached.

In terms of the high early gamma radiation fields, radiolysis, or the chemical breakdown of water by radiation, is the process of most concern. Photon radiations deposit energy to the medium through which they are passing by photoelectric compton scattering and pair production with the electrons of the medium. The primary interactions release secondary electrons that lose energy through the same physical mechanisms. The result is a cascade of electrons and secondary photons that excite and ionize the medium. In aqueous solutions, the deposited energy goes into the excitation and ionization of water molecules that decompose into a host of chemical species. Some of the most common radiolysis reactions are given below:

\[
\begin{align*}
H_2O &\rightarrow H_2O^+ \\
H_2O &\rightarrow e^- \\
H_2O &\rightarrow H_2O^* \\
H_2O^* + H_2O &\rightarrow H_3O^* + OH \\
2HO_2 &\rightarrow H_2O_2 + O_2 \\
2OH &\rightarrow H_2O_2 \\
OH + H_2O_2 &\rightarrow H_2O + HO_2 \\
\end{align*}
\]

Amounts of the above species that are produced depends upon the ionization density as differentiated with the linear energy transfer of the particular
radiation. The major radical reactions principally form molecular hydrogen, hydrogen peroxide, or reform water. Any water that enters the repository must be assumed to flow by the canisters. This is important because the H₂O₂ that would be formed by radiolysis is known to change the oxidation potential of most aqueous solutions and thus may change the expected corrosion rate and mechanisms of the canister metal (albeit in a favorable direction in some cases).

Irradiation of pure water in a closed system by low LET (linear energy transfer) particles results in a steady state with low solution concentrations of hydrogen, oxygen and hydrogen peroxide. With high LET radiation, a steady state condition is never reached or only after a long period of time. An open system leads to steady state concentrations of hydrogen peroxide with continual escape of hydrogen and oxygen; essentially, the radiation decomposes water into hydrogen and oxygen. In the presence of oxygen, hydrogen peroxide is the main radiolysis product of water. For moist air systems, radiolysis products are predominantly NO, N₂O and O₃ for temperatures above 135°C. From 120 to 135°C, NO₂, N₂O₄, H₂O and O₃ are the main products; and below 120°C, HNO₂ and H₂O are predominant. In liquid water at high radiation levels, small amounts of nitrates and nitrites will also be produced. Nitrous oxides dissolve in water to form nitric acid under certain conditions (two-phase).

For the repository, the combination of liquid water and radiation is only possible during periods of liquid water movement through it. The J-13 well water from Yucca Mountain was analyzed in 1985 by Glass, and its primary reaction with radiation was to produce the oxidizing species O₂ and H₂O₂ with small concentrations of O₂⁻ and HO₂². In summary, gamma radiation with water or dilute aqueous solutions produces a host of transient radicals, ions and stable molecular species. Other species are also generated by reactions with components of the groundwater.

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1.2 High Level Waste Canister

Having discussed some of the temperature effects and design constraints as well as the radiation sources and resulting chemical changes in the environment surrounding the waste canister, the next step is to specify the canister configuration and design parameters.

1.2.1 Current Design and Expectations

Sealed canisters will hold high level waste during handling, transportation, and storage phases of disposal. The current design is a multi-purpose canister (MPC) holding spent nuclear fuel assemblies and surrounded by a storage unit, transportation cask, or disposal container. Several MPC designs are under consideration - a legal weight truck cask for four pressurized water reactor (PWR) or nine boiling water reactor (BWR) assemblies, a medium-sized rail cask for 12 PWR or 24 BWR assemblies, and a large-sized rail MPC for 21 PWR or 40 BWR assemblies. Different designs are needed to accommodate the limitations of various reactor facilities. MPC's consist of a cylindrical shell to provide structural support and geometrical stability, two lids to form containment boundaries, a spent fuel basket to support the SNF and provide a mechanism for heat transfer, and a shield plug to keep dose rates as low as reasonably achievable.9

1.2.2 Candidate Metals

The metals under consideration for the canisters are cast iron, carbon steel, Inconel 825, and titanium grade-12. Stainless steel was proposed as a suitable container material but it has been eliminated because of uncertainty in non-uniform corrosion resistance under repository conditions.

1.2.2.1 Iron and Low Carbon Steel

The general corrosion of irons and carbon steels not subjected to radiation is controlled by the buildup of corrosion product films; however, with 1.5 Gy/hr the corrosion rate becomes 15 times higher in water. This is

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thought to be caused not only by the production of oxidizing species but also by a radiation-induced change in film morphology and protectiveness.\textsuperscript{10}

1.2.2.2 Inconel

Inconel is generally very resistant to pitting, and pits that do occur are shallow rather than deep. Inconel also resists attack by oxidizing aqueous media so it is used extensively where oxidation resistance at elevated temperatures is required. In order for Inconel to become susceptible to stress corrosion cracking, specifically damaging elements such as phosphorus or boron must reach a critical concentration by slow diffusion to grain boundaries; so to minimize cracking, control of the Inconel composition is most important.\textsuperscript{6}

1.2.2.3 Titanium Alloys

The potential failure mechanisms for titanium are crevice corrosion and hydrogen-induced cracking. Both grades 2 and 12 have been studied but grade 12 has been found to be more crevice corrosion resistant.\textsuperscript{11} The propagation of crevice corrosion on grade 2 materials depend on temperature and oxygen concentration; after the oxygen is consumed, the material repassivates. For grade 12 titanium, crevice corrosion propagation is almost independent of temperature and repassivates for temperatures less than 73°C even in the presence of excess oxygen.\textsuperscript{12}

Overall, the effect of radiation on localized corrosion appears to be specific to individual materials.

1.3 Corrosion

In determining lifetime estimates for the canisters, it is important to understand the mode of attack. The metals under consideration have different susceptibility to general corrosion and non-uniform corrosion, and

it is also necessary to consider the environment around them. Pitting and stress corrosion cracking are discussed here because they are the most likely mechanisms of failure for the candidate metals. To study corrosion, various electrochemical techniques are often used. Since non-uniform corrosion is composed of random events, an electrochemical noise technique was investigated for its suitability as an analysis tool.

1.3.1 General Corrosion

Rusting of iron and tarnishing of silver are common examples of uniform corrosion, which is characterized by a constant corrosion depth or weight loss per unit area across a surface. The rate of attack representing time-averaged values is usually shown in mm/y (millimeters per year) or gmd (grams per square meter per day) referring to metal penetration or weight loss of metal, not including any corrosion products on the surface. The initial corrosion rate will generally be greater than the subsequent rate; therefore the duration of exposure is an important parameter, and it is often not safe to extrapolate short experimental times.13

Three classifications are commonly used as a rough guideline for uniform corrosion acceptability. A material with a rate less than 0.15 mm/y is considered to have good corrosion resistance and can be used for critical components. Rates from 0.15 to 1.5 mm/y are sometimes satisfactory for non-critical parts where more corrosion is tolerable. Materials with uniform corrosion rates greater than 1.5 mm/y are generally considered unsatisfactory.6

For the prospective Yucca Mountain repository, the rate is very important because the canisters must last a minimum of 300 years and would preferably withstand penetration for 1000 years or longer. Generally, the maximum acceptable rate is found by dividing the canister wall thickness by the canister lifetime and the safety factor. For example, a 10 cm thick titanium canister expected to maintain integrity for 1000 years with a safety factor of 2.0 would have a maximum corrosion rate of 0.05 mm/yr, which must be supported experimentally to be accepted as a reasonably achievable corrosion rate in the environment expected in the repository. Canister design will consequently differ for each metal under consideration if each is to

achieve comparable lifetimes, since they will surely have varying corrosion rates. For some confidence in short term experimental results, the corrosion mechanism must also be carefully studied since 1000 year tests are impractical.

1.3.2 Non-uniform Corrosion

One localized type of corrosion is pitting, which is characterized by varying rates of attack over the surface. Corrosion in a small fixed area acting as an anode results in deep pits, while larger areas produce shallow pits. Pitting factor, illustrated in Figure 1.2, refers to the depth of pitting measured by the ratio of deepest to average metal penetration as determined by the sample's weight loss. Uniform attack results in a pitting factor of unity.

For pitting to occur on a passive surface, the corrosion potential must be greater than a critical potential. Increasing the fraction of alloyed chromium, nickel, molybdenum and rhenium in stainless steels shifts the critical potential and increases the resistance to pitting. When pitting does occur, a passive-active cell is created as seen in Figure 1.3. This produces a high current density and a high corrosion rate at the pit; meanwhile, the surrounding surface is polarized to potentials below the critical value. Chloride ions, if present, would enter the pit concentrate and produce an acid solution. A high Cl\(^-\) concentration and low pH environment keep the pit active, while the high specific gravity of the corrosion products causes leakage out of the pit; breakdown of the passive layer occurs where the metal surface is contacted. When the pit surface is repassivated, pitting stops. Dissolved oxygen or passivator ions are needed, but successful repassivation depends on pit geometry and flow rate of the surrounding solution.

Several methods are commonly used to reduce or avoid pitting. Cathodic protection at a potential below the critical value can be accomplished by using an applied current or coupling in a conductive medium to a greater area of zinc, iron or aluminum. Additional anions such as OH\(^-\) or NO\(_3\)\(^-\) can be added to chloride environments, or the oxygen concentration can be reduced. Temperature can be adjusted to discourage pitting corrosion. For example, the lowest possible operating temperature should be used for stainless steel type 304. In an aerated 4% NaCl solution, this metal experiences maximum weight loss by pitting at 90°C.\(^{14}\)

Uniform Corrosion Depth D

Original Surface

Pitting Depth P

Metal

Pitting Factor = P/D

Figure 1.2. Pitting Factor as a Function of Pit Depth and Uniform Attack

NaCl Environment

Oxygen Sites

Chlorides

Stainless Steel

Figure 1.3. Passive-Active Cell
In the repository, there are several chemical factors that may contribute to or alleviate pitting attack of the canisters such as anion concentration, radiation and pH. Since water contacting the canisters is expected to evaporate and rise potentially to condense and flow into the repository again, the concentration of anions near the canisters would be expected to increase due to this evaporation effect. After the temperature drops below the boiling point, water near the canisters will dissolve these additional anions; and this water could be highly corrosive and thus enhance pitting. Although pitting is not directly caused by radiation, a pit that has already been initiated may have an increased propagation rate because the water inside the pit may have a higher concentration of \( \text{H}_2\text{O}_2 \) since the innermost point of the pit is closer to the radiation source and has a slightly higher gamma flux, thus causing a differential electrochemical condition.

The effect of pH on the corrosion rate depends on the metal under consideration. For aluminum and zinc, the corrosion rate increases at both high and low pH; but for iron and steel, the penetration rate actually decreases above a pH of about 10.

1.3.3 Electrochemical Analysis

Electrochemistry is the study of the chemical response of a system to an electrical stimulation. When a metal is immersed in a given solution, electron exchange reactions occur at the surface of the metal causing it to corrode. Since this involves electrochemical oxidation and reduction reactions, it is useful to study and measure the corroding systems with electrochemical methods. The technique explained in this thesis used three electrodes - two working electrodes and a reference electrode. The working electrode is the electrochemical term for the specimen where the reactions of interest take place. The reference electrode is a stable half-cell against which the potential of the working electrode is measured. In an electrochemical experiment, four parameters are of interest - potential, current, charge and time. Different combinations of these parameters and electrode types create a long list of possible techniques, including voltammetry, polarography, cyclic voltammetry, chronoamperometry, chronopotentiometry and more.\(^{15}\) Electrochemical noise techniques are unique because they provide an entirely

passive analysis tool. No current or voltage is applied to the system under test.

Electrochemical noise techniques have become widely used in various applications. Stewart et. al. used current pulses to detect the initiation, temporary propagation and repassivation of intergranular stress corrosion cracks in sensitized stainless steel under BWR conditions.\textsuperscript{16} For a totally random current signal (as is true for pitting), impedance techniques have not been found to be successful, and only analysis of the current fluctuations will produce information of the processes involved. Gabrielli and Keddam used this sort of electrochemical noise analysis to study active and inhibited corrosion of iron, aluminum alloys and stainless steel.\textsuperscript{17} Blanc measured electrochemical noise by a cross correlation method in studying $1/f$ noise or flicker noise.\textsuperscript{18} Noise signals can also give information about the magnitude and decay time of electrode processes such as the onset of pitting or the effect of corrosion inhibitors. Bertocci measured electrochemical noise and separated the deterministic response from random current fluctuations when examining aluminum at and below the pitting potential.\textsuperscript{19} Bertocci and Kruger also analyzed the difference in noise levels for amorphous and crystalline Fe-Cr-Ni alloys, and they showed that the breakdown of the passive film was different for the two forms.\textsuperscript{20} Hladky and Dawson measured corrosion with electrochemical $1/f$ noise, and they found a correlation between the rate and mode of corrosion attack and fluctuations of the corrosion potential. They predicted the possibility of detecting pitting and crevice attack based on non-perturbative electrochemical monitoring.\textsuperscript{21}

1.4 Project Purpose and Goals

This project was designed to evaluate passive electrochemical noise techniques for measuring pitting and corrosion characteristics of candidate materials under prototypical repository conditions. Experimental techniques were also developed and optimized for measurements in a radiation environment. The specific associated goals include:

- designing an appropriate experimental test apparatus,
- replicating the radiation level, chemical environment, and temperature for a cold repository scenario,
- determining the effects of temperature on pitting and electrochemical noise data,
- determining the effects of radiation on pitting and electrochemical noise data,
- determining the validity of simulated irradiation testing,
- comparing data and trends for different metals,
- critiquing the analysis techniques for use in passive monitoring applications,
- and critiquing the analysis method as a predictive tool.
2 Experimental Components

2.1 Overview

An experimental apparatus was designed and built to make electrochemical noise measurements with and without the presence of a gamma radiation field. The experimental assembly consisted of a reference electrode, a working electrode and a counter electrode. To use electrochemical noise techniques for analysis, the current was measured across the working and counter electrodes, and the voltage was measured across the reference and counter electrodes.

The working, or test electrode, was made of one of the candidate materials described in Section 2.2.1., and the counter electrode was an Inconel 825 specimen. The reference electrode was a glass-body, sealed, single-junction Ag/AgCl electrode with a gel filling for use up to 120°C. Electrode preparation was accomplished by initial surface sanding, and it was then set in an epoxy insulator to protect the soldering point and to prevent the electrodes from touching each other during operation. After final sanding, the surface was photographed. All three electrodes were situated inside a stainless steel can through which water typical of that found at Yucca Mountain was slowly pumped.

Gamma radiation results in the decomposition of H_2O and the formation of the primary long-lived oxidizing species H_2O_2. To monitor the buildup of H_2O_2 in the experiment, measurements were made out-of-assembly using ampoules for photometric analysis of hydrogen peroxide. Water temperature was maintained by a proportional integral derivative (PID) temperature controller with a thermocouple adjacent to the electrodes and a flexible fiberglass heating tape around the outside of the assembly. A pressure transducer was located on the outlet water line to monitor any pressurization of the assembly for safety purposes. This entire setup fit within an outer aluminum can which was sealed and then inserted into the gamma radiation field in the MITR II spent fuel pool. Tests were conducted, and all data was sent to the data acquisition program, LabVIEW 2, for storage and analysis.

The electrodes used in this experiment are discussed in Section 2.2. This includes a description of the candidate metals studied and the surface preparation procedure developed for them. Section 2.3 discusses the main
structural units of the experimental assembly which are the stainless steel inner can and the aluminum outer can. The external apparatus is described in Section 2.4 including discussion of the synthetic water production, gamma radiation source and dose measurements, temperature control system, and pressure monitoring for safety purposes. Section 2.5 describes data acquisition. Microscopy was used to compare surface defects, and LabVIEW 2 was used to store and analyze the electrochemical noise measurements. The design and capabilities of LabVIEW 2 are discussed, and the methods of data acquisition and analysis are described. Section 2.6 puts the whole picture together and describes the experimental procedures, drawing on the descriptions in the previous sections.

2.2 Electrodes

The Yucca Mountain Site Characterization Project has selected potentially suitable metals for use in fabrication of the high level waste storage canisters. Currently, these metals are cast iron, carbon steel 1018 or 1020, Inconel 825 and titanium code-12. Tables 2.1-5 give more information on these metals' chemical and physical properties.

2.2.1 Candidate Metals

Gray cast iron is easy to cast sound and readily machinable. It is not usually considered weldable and is incapable of cold forming.\[^{22}\] Cast iron remains an option despite its rapid corrosion rate because it has been widely used for many years and therefore has more long-term data available to better assist in making 300 year canister performance predictions defensible. Cast iron samples for our project were donated by the Charlotte Brothers Iron Foundry, Inc. of Blackstone, MA as 3/8" plate. Table 2.1 shows representative properties for SAE Grade G3500 and ASTM Class 35 gray cast iron.\[^{23}\]

Carbon steel also has relatively less favorable corrosion behavior but many years of experience. Table 2.2 shows composition limits for the sample of 1/2" 1018 carbon steel rod and generic physical properties for carbon steel.\[^{22}\] Impurities in our 3/8" 1020 carbon steel plate sample are shown in Table 2.3.


Inconels as a general class of materials are relatively new compared to carbon steel and cast iron, but have excellent corrosion resistance and would probably not fail by general corrosion. Non-uniform modes of attack, such as stress corrosion cracking, are of greater concern for Inconels. The chemical analysis and physical properties for the 1/2" Inconel 825 rod used in this experiment are in Table 2.4.

Titanium is exceptionally resistant to general corrosion but it is also a relatively new material, and it is much more difficult to weld and machine than any of the iron or nickel-based alloys. Material tests for the 1/8" titanium grade-12 plate used in this experiment are in Table 2.5.

<table>
<thead>
<tr>
<th>Table 2.1. Representative Gray Cast Iron Data</th>
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</thead>
<tbody>
<tr>
<td><strong>Composition Limits (%)</strong></td>
</tr>
<tr>
<td>SAE Grade</td>
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<tr>
<td>G3500</td>
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</table>

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
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</thead>
<tbody>
<tr>
<td>ASTM Class</td>
</tr>
<tr>
<td>35</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2.2. Representative Carbon Steel 1018 Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition Ranges (%)</strong></td>
</tr>
<tr>
<td>SAE #</td>
</tr>
<tr>
<td>1018</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Physical Properties</th>
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</thead>
<tbody>
<tr>
<td>Yield Strength</td>
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<td>50,000 psi</td>
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<tr>
<th>Table 2.3. Carbon Steel 1020 Impurities for Sample A302B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Actual %</strong></td>
</tr>
<tr>
<td><strong>Maximum %</strong></td>
</tr>
</tbody>
</table>
Table 2.4. Inconel 825 Analysis Results for Sample HH6756FG

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th></th>
<th></th>
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<th></th>
<th></th>
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<th></th>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>Mn</td>
<td>P</td>
<td>S</td>
<td>Si</td>
<td>Ni</td>
<td>Cr</td>
<td>Cu</td>
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<tr>
<td>%</td>
<td>0.01</td>
<td>0.34</td>
<td>0.001</td>
<td>0.10</td>
<td>43.9</td>
<td>21.86</td>
<td>2.05</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>Cb</td>
<td>Sn</td>
<td>Fe</td>
<td>Al</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.86</td>
<td>28.07</td>
<td>0.09</td>
<td></td>
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<td></td>
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</table>

Table 2.5. Titanium Code-12 Material Tests for Sample T-0300

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th></th>
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<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>Fe</td>
<td>N</td>
<td>Mo</td>
<td>H</td>
<td>O</td>
<td>Ni</td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>0.018</td>
<td>0.11</td>
<td>0.004</td>
<td>0.29</td>
<td>0.005</td>
<td>0.13</td>
<td>0.82</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Mechanical Tests ‡</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Yield-L</td>
<td>Yield-T</td>
<td>Tensile-L</td>
<td>Tensile-T</td>
<td>Elong.-L</td>
<td>Elong.-T</td>
<td></td>
<td></td>
</tr>
<tr>
<td>62 ksi</td>
<td>83 ksi</td>
<td>87 ksi</td>
<td>96 ksi</td>
<td>22 %</td>
<td>20 %</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

‡ L indicates longitudinal orientation and T indicates transverse orientation

2.2.2 Sample Preparation

Plates and rods of the candidate materials were cut into 1 cm squares or circles depending on the shape of the initial sample, and a 1/16" hole was drilled into one side. An identification number was stamped on the back of the electrode opposite the side chosen for analysis. Smoothing of the surface was accomplished with a horizontal dry/wet grinder using wheels of grit 120, 1000 and 6000 after which final polishing was done with 1 micron alumina powder on a cloth wheel. Mineral insulated cable, with a double strand of stainless steel wire insulated by MgO and surrounded by an outer layer of stainless steel, was then soldered to the electrode after inserting the inner stainless steel strands into the 1/16" hole in the electrode. This connection and all exposed regions of the electrode except the face under consideration were then insulated with Varian® vacuum epoxy cement. Optical microscope surface pictures with 20X magnification were taken.

2.3 Structural Units

The experimental apparatus consisted of an inner can containing the electrodes and flowing water for the experiment, and an outer can to isolate the electronics and heater from the water in the spent fuel pool.
2.3.1 Inner Can

The components for the inner can were 304 stainless steel (SS). This consisted of a 3/4" coupling, a 1 1/2" cap, a 3/4" x 6" pipe, a 1 1/2" x 6" pipe, and a 3/4" to 1 1/2" reducer. On each pipe section, a 1/4" elbow was welded 1/2" above the bottom threads to form connections for water lines as shown in Figure 2.1. The inlet line entered the large pipe, and the outlet line left from the smaller pipe. Before assembling, these parts were heat treated at 800°C in air for about four hours to reduce corrosion of the vessel.

Inside the can, a 304 SS circular perforated frame was used to ensure correct placement of all electrodes and the thermocouple as illustrated in Figure 2.2. Extra holes were drilled to allow for flow through the frame.

In Figure 2.1, a 1/4" 304 SS tee on the outlet water line sent flow to the pressure snubber and transducer. At the end of the outlet water line, a 1/4" 316 SS valve controlled the pressure inside the vessel. At the top of the inner can, there was a Conax 3/4" 304 SS pressure fitting that allowed access for six 1/8" probes. The fitting seal was Viton for use from -10° to 500°F, up to 10,000 psi, and up to 2 x 10⁸ Rads. The seal was secured with an applied torque of 120-130 ft-lbs. 24 Since the electrodes and thermocouple only used four of the six available probe openings, extra mineral-insulated cable was placed in the remaining holes. When assembling the inner can, Loctite PST nuclear grade pipe sealant was used at all connection points. This was a low halogen-low sulfur sealant with certificate of test containing 200 ppm maximum chlorine and 1500 ppm maximum sulfur. It was for use from -55° to 149°C and up to 2 x 10⁸ Rads. 25 After initial sealing of all connections, the can was designed to only be taken apart at the two points indicated in Figure 2.1 to remove the electrodes inside. The reducer-to-large pipe point was disconnected and the Conax fitting was loosened to free the thermocouple and electrode wires. An aluminum plate 1 3/4" by 3 5/8" with a central hole of 1" diameter was placed beneath the top of the Conax fitting and allowed the inner can to hang at the correct level within the outer can.

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Figure 2.1. Inner Can Components
Figure 2.2. Inner Can Internals
2.3.2 Outer Can

The outer can was made primarily from 6061 aluminum and 304 SS. The pieces in the bottom section were all aluminum - a 3" diameter plate, a 3" x 30" pipe, a 9" x 4" square box, a 4" square plate with a 3" diameter central hole, and four 1" angles with a 3/8" diameter hole. These were welded together as shown in Figure 3.3. The top section consisted of stainless steel - a 6" square plate with four couplings welded through it for water and instrument lines. There were also 3/8" holes that lined up with the similar holes in the angles on the bottom section. To the top of the stainless steel plate, two 1/2" 304 SS tubes for instrumentation wires and two 1/4" 304 SS tubes for water lines were connected. The height of these tubes was approximately 4' to allow for flexible rubber tubing to be connected outside the gamma field. To attach the upper and lower sections, a rubber gasket was placed between them, and 3/8" by 2" bolts were inserted through the four holes and tightened with nuts and washers. To facilitate immersing this unit under twenty feet of water in the spent fuel pool, a lead brick was placed in the bottom of the outer can.

2.4 External Apparatus

2.4.1 Chemical Environment

Water chemistry for the fluid flowing by the electrodes was meant to simulate the expected environment in the Yucca Mountain repository. Water from a well near Yucca Mountain, J-13, has already been well characterized, and its components are listed in Table 2.6.26 To prepare similar J-13 water in the laboratory, solutions of MgSO$_4$, K$_2$SO$_4$, Li$_2$SO$_4$, NaNO$_3$, NaF, NaCl, Na$_2$CO$_3$, Na$_2$SO$_4$, SiO$_2$ and CaCO$_3$ were mixed in the correct concentrations, and an ICP was used to verify that the final product was within reasonable error margins. Potassium and sodium were tested and found to be 5.11 ppm and 39.8 ppm, respectively; these values were both less than 10% away from the desired concentrations. Because the carbonate level in the simulated water was less than that found in the characterized J-13 water, the pH was affected and nitric acid was added to adjust the solution.

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Figure 2.3. Outer Can Components
into the pH 7-8 range. Another difficulty with preparation of J-13 water was the low solubility of SiO$_2$ and CaCO$_3$ that required vigorous and lengthy stirring of the prepared solution.

### Table 2.6. Composition of J-13 Well Water

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (ppm)</th>
<th>Component</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>44</td>
<td>HCO$_3^-$</td>
<td>125</td>
</tr>
<tr>
<td>K$^+$</td>
<td>5.1</td>
<td>NO$_3^-$</td>
<td>9.6</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1.9</td>
<td>SO$_4^{2-}$</td>
<td>18.7</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>12.5</td>
<td>PO$_4^{3-}$</td>
<td>0.12</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>58</td>
<td>H$_2$O$_2$</td>
<td>-</td>
</tr>
<tr>
<td>F$^-$</td>
<td>2.2</td>
<td>Al$^{3+}$</td>
<td>0.012</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>6.9</td>
<td>Fe$^{2+}$</td>
<td>0.006</td>
</tr>
</tbody>
</table>

### 2.4.2 Radiation Source

The MITR II spent fuel pool served as the radiation source for this project, with usage time donated by the MIT Nuclear Reactor Laboratory. The storage pool was a 21 foot deep steel-lined concrete tank with an 8 foot inner diameter used to store spent fuel, control blades and other irradiated core components. It was filled with high purity deionized water to remove the decay heat and protect personnel working above the pool. Three storage racks, consisting of a five by five matrix of open-ended boxes constructed of an aluminum-cadmium-aluminum sandwich, rested on the bottom of the pool. The boxes were 3.75" square on the inside, and experiment tubes could be placed in any empty storage box. The position for this project is shown in Figure 2.4.

The radiation level for a sample depended on the burnup and decay of the surrounding spent fuel elements; for the SFP position used, the adjacent elements and their operating history are summarized in Table 2.7. Elements MIT 08 and 19 have very low burnup because they experienced clad failure early in their life, so they also have longer decay times. The dose level was determined using radiochromic film, an aminotriphenyl methane dye.

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derivative that undergoes radiation-induced coloration by photo ionization. The film was dose rate independent to $10^{15}$ Rads/sec and had only a small temperature sensitivity. It had a linear response to ionizing radiation over a wide range and was independent of energy down to a few keV. One centimeter squares of film were exposed to the source, and then a photometer was used to read the change in transmission of the film. Calibration services were provided courtesy of the University of Lowell Radiation Laboratory. The radial distribution of the dose rate in our sample position peaked slightly above the center at 30,000 Rads/hr as shown in Figure 2.5.
Table 2.7. Spent Fuel Elements Data as of 1-1-94

<table>
<thead>
<tr>
<th>Element #</th>
<th>Burnup (MWD)</th>
<th>Decay Time (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIT 01</td>
<td>3654.54</td>
<td>3.98</td>
</tr>
<tr>
<td>MIT 03</td>
<td>3733.01</td>
<td>2.73</td>
</tr>
<tr>
<td>MIT 06</td>
<td>3947.48</td>
<td>2.73</td>
</tr>
<tr>
<td>MIT 08</td>
<td>943.92</td>
<td>10.17</td>
</tr>
<tr>
<td>MIT 19</td>
<td>570.01</td>
<td>7.21</td>
</tr>
</tbody>
</table>

2.4.3 Temperature and Pressure Monitoring

The water temperature inside the sample assembly was maintained by a heater wrapped around the inner can and a thermocouple inside the can, with both connected to a temperature controller located out of pool. The flexible electric heating tape had fine-strand resistance wires insulated with braided fiberglass, knitted into flat tapes with Fibroxtm fiberglass yarns and covered with heavy fiberglass fabric covering. The heater tape was a 240 VAC
model of 1" width and 72" length with ties at each end to secure it and 24" insulated lead wires emerging from opposite ends for connection to the power source. The thermocouple was a type K Chromega™-Alomega™ quick-disconnect probe with a grounded stainless steel 304 sheath 18" in length and 1/8" in diameter. It was recommended for use from -200 to 1260°C in flowing corrosive liquids when a faster response is needed. The temperature controller was a 1/16 DIN auto-tune controller with PID control and 0.1°C resolution for thermocouple input.

For pressure monitoring (a necessary safety precaution, although all testing was performed near atmospheric pressure), a snubber and transducer on the outlet water line were connected to a digital panel meter. The snubber contained porous metallic elements and was rated for water and light oils (30 to 225 S.S.U.) up to 15,000 psi. Its housing was SS 303 and the porous discs were SS 316. The transducer had a chemical vapor deposited polysilicon strain gage and was reverse polarity protected. Its operating temperature was from -40° to 125°C. The meter was a 3 1/2 digit panel meter consisting of a main assembly and a plug-in strain gauge/excitation supply board. An electrically floating supply powered transmitters, active transducers and bridges. It offered a high-impedance precision preamplifier with programmable gains of 1, 3, 10, 30 and 100 to provide resolutions of 1000, 300, 100, 30 and 10 mV/count respectively. Typical offset drift was only 0.3 mV/°C, and the excitation maximum output was 20 mA at 24 V dc.

2.5 Data Acquisition

2.5.1 Microscopy

After the electrodes completed the sample preparation phase, they were photographed with an optical microscope of 20X magnification using Polaroid® pictures. The film was black and white PolaPan® ISO 400/27° 4x5 instant sheet film of medium contrast. It had panchromatic spectral

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sensitivity, and its print resolution was 20-25 line pairs/mm. The photos were typically processed for 20 seconds in an ambient room temperature of 70°C before the developer was removed and the prints were covered with a caustic paste to preserve their quality. The border of the photos was cut away and a montage was constructed; usually six or eight photos were required to cover the entire electrode face. Typical before and after montages of the surface of a carbon steel electrode are shown in Figures 2.6 and 2.7.

2.5.2 Pitting Factor

As defined in Section 1.3.2, pitting factor refers to the ratio of deepest to average metal penetration. To prepare an electrode for pit depth determinations, the epoxy covering the back was sanded flat. This allowed the width of the electrode from face to back to be measured with a ten-thousandths Starrett® micrometer caliper. The face of the electrode was then photographed and a small portion of the face was sanded away (approximately 0.0002-0.0004 inches). This process of micrometer measurement, photography, and surface sanding was repeated until no more pits were visible on the surface. Then the photographs were input as layers to form a three-dimensional electrode model using a Kurta XGT®/ADB graphics digitizing tablet. AutoCAD®, a general purpose Computer Aided Design (CAD) program for preparing two-dimensional drawings and three-dimensional models, was used to manipulate the layers to represent structure of the pits. The AutoCAD® Advanced Modeling Extension™ Release 2.1 software was used to mathematically find the percentage of area on each layer composed of pits.

This corrosion analysis technique was used to calculate the pitting factor as well as the percentage of surface area corroded at each layer, the average depth of each layer, and the estimated corroded pitting volume of each layer.

2.5.3 LabVIEW

Data acquisition and instrument control procedures were automated for ease of use and reproducibility. LabVIEW is a high-level programming environment that allows for simplification of the automating procedures.
Figure 2.6. Carbon Steel Electrode Before Test

Figure 2.7. Carbon Steel Electrode After Test
2.5.3.1 Design and Capabilities

LabVIEW uses virtual instruments that are software constructions that have characteristics of actual instruments. A virtual instrument (VI) has a front panel displayed on the computer screen with controls and indicators which are operated by the keyboard and mouse, a block diagram representing the assembly of electronic components in a real instrument, and a calling interface using an icon/connector for communication with the computer and other VI's. LabVIEW creates a friendly environment by replacing the lines of code generally associated with programming languages by intuitive graphic objects. These objects that look like the knobs and switches that control real instruments or the meters and lights that indicate real values are arranged on the front panel by the user. The block diagram is the VI's source code, and is easily connected (wired) together. The icon/connector represent the VI as a subroutine call statement when the VI is used as a subVI within another VI's block diagram.34

2.5.3.2 Voltage and Current Data Acquisition and Analysis

Voltage measurements were taken with an HP 34401A multimeter, and a Keithley 485 autoranging picoammeter was used for current measurements. These both communicated with a Macintosh LCIII via a National Instruments GPIB-SCSI-A box. The VI written to record this data is shown in Figure 2.8. For controls, it has on/off buttons and delays for each instrument. The delay allowed the user to specify the time in milliseconds between instrument readings. The VI also indicates the values of the last readings and maintains a strip chart with a scroll bar for both the voltage and current. The block diagram calls up two subVI's; one operates the multimeter and the other controls the picoammeter, as shown in Figure 2.9. These have their own front panels, block diagrams and subVI's that are customizations of National Instruments software. The multimeter and picoammeter subVI's do such things as open and close their respective instruments, read and write data from the instrument to the computer, and check for processing errors. Figure 2.10 shows the hierarchy of all these VI's.

The front panels and block diagrams of all the VI's used for this project are included in Appendix A.

Front Panel

Figure 2.8. Data Acquisition VI Front Panel

Block Diagram

Figure 2.9. Data Acquisition VI Block Diagram
2.5.3.3 Spectral Density Analysis

Analysis was done with a separate VI whose front panel is shown in Figure 2.11. This VI used National Instruments analysis programs to calculate the standard deviation (σ) and the mean (μ) for both the current and voltage data using the following formulas:

$$\sigma = \sqrt{\frac{1}{n} \sum_{i=0}^{n-1} (x_i - \mu)^2}$$

and

$$\mu = \frac{1}{n} \sum_{i=0}^{n-1} x_i$$

where n is the number of elements in the input sequence X, which is either the current or voltage data in this case.

To reconstruct all or part of the current strip chart (now on an xy graph), the user specified the appropriate start and end data points, which were accessed from the voltage and current data acquisition subVI, and could then manipulate the new graphical display and supply comments about the run. An error would result if the data could not be retrieved or if an invalid data point number was entered.
For frequency analysis, the power spectral density (psd) of the entire current trace for each run was calculated in decibels within the frequency range of interest using the following equation:

$$psd = \log\left(\frac{1}{n} \cdot |F\{X\}|^2\right)$$

where $F\{X\}$ is the Fourier Transform of the input sequence $X$ and $n$ is the number of samples. The minimum frequency of interest is the inverse product of the number of samples and the time increment, and the maximum frequency is the inverse of twice the time increment. Analysis of the power spectral density of the current data is interpreted to indicate localized corrosion in the low frequency range and general corrosion in the higher frequency range.

Figure 2.11. Spectral Density Analysis VI Front Panel
2.6 Experimental Procedures

The first step in all tests was sample preparation. The electrodes to be used were cut into the desired shape, and their surfaces were polished as described in Section 2.2.2. Instrumentation wires were soldered onto them and the edges were insulated with epoxy. The two test electrodes and the reference electrode were positioned in the inner stainless steel can as shown in Figures 2.1 and 2.2 with the thermocouple. The test chamber was sealed with a sealant and was cured for 24 hours before actual testing began.

The flexible heater was placed around the bottom section of the can and surrounded with insulation. This entire unit was put into the outer aluminum can, and the pressure and temperature monitoring apparatus was attached as described in Section 2.4.3. The electrode instrument wires were connected to the voltmeter and picoammeter, which interfaced via the SCSI box to the computer and the data acquisition system discussed in Section 2.5.3. Finally, the water inlet and outlet lines were connected to the flowmeter but flow was not initiated.

As testing began, the data acquisition program began running in continuous mode. Flow by siphoning was started and the heater was turned on. For runs done with radiation, the entire apparatus was inserted into the position in the spent fuel pool shown in Figure 2.4. Testing then continued until for the desired length of time.

After testing was completed, the heater was turned off and data acquisition was stopped. For radiation testing, the apparatus was removed from the spent fuel pool. Flow continued until the inner can had cooled down somewhat to facilitate disassembly. All instrumentation wires were disconnected, the insulation and heater were removed, and the electrodes were taken out of the inner can.

The physical corrosion data was analyzed as described in Section 2.5.2 to determine the pitting factor, the percentage of surface area corroded at each layer, the average depth of each layer and the estimated corroded pitting volume of each layer. The current traces from the electrochemical noise data were analyzed to find the mean value, standard deviation and the area under each curve. Spectral density analysis was also used with the current data as discussed in Section 2.5.3.3 to find the slope of the psd curve and information about the relative localized and general corrosion activity.
Chapter 3 presents results of the experimental techniques and analyses described in Chapter 2. Section 3.1 presents results and discussion of tests done at various temperatures and the effect on the localized corrosion behavior of these samples. Results comparing the effect of irradiation on localized corrosion are shown in Section 3.2, and Section 3.3 has results for similar tests done with peroxide to simulate radiation. Section 3.4 compares localized corrosion characteristics for different metals. Section 3.5 discusses loading geometry for all tests.

3.1 Temperature Comparisons

3.1.1 Experimental Parameters

For the temperature comparison runs, Inconel 825 was used as the counter electrode because it was found to be essentially inert relative to carbon steel and cast iron in the environment studied. Tests were run at temperatures of 25, 50, and 90°C for 24 hours. All data was taken with a 2 second delay resulting in approximately 20,000 data points per run accounting for time required for data acquisition. These tests were completed in the laboratory without exposure to radiation.

3.1.2 Pitting Analysis

As described in Chapter 2, detailed analyses were performed to determine the degree of pitting at various depths below the surface of the metal. Microscopy Polaroid® pictures are presented in Appendix B, and the representative layers are shown for the carbon steel electrodes in Appendix C. Table 3.1 lists the percentage of area corroded, the average depth, and an estimated corroded volume for each layer. The depth of the first layer is assumed to be the depth of uniform corrosion for pitting factor calculations. The pitting factor is numerically estimated as the depth of the deepest pit, corresponding to the depth of the final layer, divided by the depth of uniform corrosion.
Table 3.1. Corrosion Data for Temperature Comparison Electrodes

<table>
<thead>
<tr>
<th>Layer</th>
<th>Percentage of Area Corroded</th>
<th>Average Layer Depth (in)</th>
<th>Estimated Volume Corroded (in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon Steel Electrode for 90°C Test - Pitting Factor = 5.52</td>
</tr>
<tr>
<td>1</td>
<td>24.52</td>
<td>1.04 e-3</td>
<td>4.5 e-5</td>
</tr>
<tr>
<td>2</td>
<td>6.38</td>
<td>1.60 e-3</td>
<td>7.0 e-6</td>
</tr>
<tr>
<td>3</td>
<td>1.56</td>
<td>2.36 e-3</td>
<td>2.3 e-6</td>
</tr>
<tr>
<td>4</td>
<td>0.57</td>
<td>3.44 e-3</td>
<td>1.2 e-6</td>
</tr>
<tr>
<td>5</td>
<td>0.08</td>
<td>5.74 e-3</td>
<td>3.6 e-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon Steel Electrode for 50°C Test - Pitting Factor = 1.95</td>
</tr>
<tr>
<td>1</td>
<td>15.15</td>
<td>1.74 e-3</td>
<td>4.9 e-5</td>
</tr>
<tr>
<td>2</td>
<td>3.08</td>
<td>2.18 e-3</td>
<td>2.7 e-6</td>
</tr>
<tr>
<td>3</td>
<td>1.32</td>
<td>2.90 e-3</td>
<td>1.9 e-6</td>
</tr>
<tr>
<td>4</td>
<td>0.12</td>
<td>3.40 e-3</td>
<td>1.2 e-7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Carbon Steel Electrode for 25°C Test - Pitting Factor = 1.49</td>
</tr>
<tr>
<td>1</td>
<td>8.93</td>
<td>1.58 e-3</td>
<td>2.6 e-5</td>
</tr>
<tr>
<td>2</td>
<td>0.60</td>
<td>1.76 e-3</td>
<td>2.1 e-7</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>2.36 e-3</td>
<td>4.7 e-8</td>
</tr>
</tbody>
</table>

3.1.3 Current Analysis

The current traces for the three runs are shown in Figure 3.1. The increased temperature produces a higher mean value as expected. The 50 and 90°C tests have similar mean current values, while the mean value of the 25°C run is only about a third the magnitude. The standard deviation for the 90°C run is also much larger than either of the others. The mean current value, standard deviation and area under each curve are listed in Table 3.2.

The power spectrums for the temperature comparisons are shown in Figure 3.2. The 25 and 50°C runs have very similar localized corrosion behavior in the low frequency range. The 90°C test experienced the highest corrosion activity along the entire frequency range. All of the power spectrums trend upwards as they reach the highest frequency in response to the influence of the heater current which was not completely eliminated.
Figure 3.1. Current Data for Temperature Comparisons

Figure 3.2. Power Spectrums for Temperature Comparisons
<table>
<thead>
<tr>
<th>Run Description</th>
<th>Mean Current Value (A)</th>
<th>Standard Deviation (A)</th>
<th>Area Under Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C</td>
<td>7.02 e-5</td>
<td>2.71 e-5</td>
<td>1.40</td>
</tr>
<tr>
<td>50°C</td>
<td>6.64 e-5</td>
<td>6.51 e-6</td>
<td>1.33</td>
</tr>
<tr>
<td>25°C</td>
<td>2.26 e-5</td>
<td>4.74 e-6</td>
<td>0.45</td>
</tr>
</tbody>
</table>

### 3.2 Radiation Comparisons

#### 3.2.1 Experimental Parameters

For the runs to compare effects of irradiation, titanium grade-12 was used for both the counter and working electrodes. All tests were done at 90°C for 24 hours. Data was taken with a 5 second delay resulting in approximately 12,000 data points for the irradiated run and a 10 second delay resulting in approximately 6,000 points for the laboratory run.

The hydrogen peroxide concentration was monitored on the outlet water flow line throughout the test. After 24 hours, it reached ~3 ppm as shown in Figure 3.3. Although this appeared to be approaching a maximum value, the concentration may have increased further if the test assembly had remained in the spent fuel pool longer. Since the peroxide concentration was measured out-of-pool after flowing through 20 feet of tubing, the actual concentration at the electrode surface would be greater.

![Figure 3.3. Hydrogen Peroxide Concentration Buildup in the SFP](image)
3.2.2 Pitting Analysis

None of the titanium samples showed any visible surface deformation after any of the tests. Figure 3.4 shows the surface before a run and Figure 3.5 shows it after the irradiated run. Since no pitting occurred, the pitting factor and associated corrosion analysis data could not be calculated.

3.2.3 Current Analysis

The current traces for the two runs are shown in Figure 3.6. Both runs show very few oscillations after the initial heatup regime, but the mean current value is much lower for the irradiated run. The mean value, standard deviation and area under each curve are listed in Table 3.3.

<table>
<thead>
<tr>
<th>Run Description</th>
<th>Mean Current Value (A)</th>
<th>Standard Deviation (A)</th>
<th>Area Under Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>in lab</td>
<td>7.17 e-8</td>
<td>4.48 e-8</td>
<td>1.43 e-3</td>
</tr>
<tr>
<td>in SFP</td>
<td>2.88 e-9</td>
<td>5.98 e-9</td>
<td>5.77 e-5</td>
</tr>
</tbody>
</table>

The power spectrums for the radiation comparisons are shown in Figure 3.7. Although both psd curves have similar overall shapes, the psd for the run in the spent fuel pool shows much less activity in both the localized and general corrosion regions.

3.3 Simulated Radiation Comparisons

3.3.1 Experimental Parameters

For testing to compare effects of simulated irradiation, carbon steel 1020 was used for both the counter and working electrodes. All tests were done at 90°C for 24 hours. Data was taken with a 2 second delay resulting in approximately 20,000 data points per run accounting for time required for data acquisition. Hydrogen peroxide was added to the reservoir for the inlet water line to maintain an inlet concentration of 1 ppm. After flowing through the heated chamber, the outlet concentration was <0.1 ppm.
Figure 3.4. Titanium Electrode Before Testing

Figure 3.5. Titanium Electrode After Testing
Figure 3.6. Current Data for Radiation Comparisons

Figure 3.7. Power Spectrums for Radiation Comparisons
3.3.2 Pitting Analysis

The layers are shown for each carbon steel electrode in Appendix C. Table 3.4 lists the percentage of area corroded, the average depth, and an estimated corroded volume for each layer. The pitting factor determined from the deepest pit on each electrode is also given.

Table 3.4. Corrosion Data for Simulated Radiation Comparison Electrodes

<table>
<thead>
<tr>
<th>Layer</th>
<th>Percentage of Area Corroded</th>
<th>Average Layer Depth (in)</th>
<th>Estimated Volume Corroded (in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.35</td>
<td>1.40 e-4</td>
<td>5.8 e-6</td>
</tr>
<tr>
<td>2</td>
<td>1.44</td>
<td>5.40 e-4</td>
<td>1.5 e-6</td>
</tr>
<tr>
<td>3</td>
<td>0.29</td>
<td>1.02 e-3</td>
<td>3.7 e-7</td>
</tr>
<tr>
<td>4</td>
<td>0.02</td>
<td>1.58 e-3</td>
<td>2.5 e-8</td>
</tr>
</tbody>
</table>

Carbon Steel Electrode for \( w/ \text{H}_2\text{O}_2 \) - Pitting Factor = 8.12

<table>
<thead>
<tr>
<th>Layer</th>
<th>Percentage of Area Corroded</th>
<th>Average Layer Depth (in)</th>
<th>Estimated Volume Corroded (in³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.68</td>
<td>5.00 e-4</td>
<td>1.9 e-5</td>
</tr>
<tr>
<td>2</td>
<td>2.63</td>
<td>1.28 e-3</td>
<td>5.1 e-5</td>
</tr>
<tr>
<td>3</td>
<td>0.49</td>
<td>2.84 e-3</td>
<td>1.9 e-6</td>
</tr>
<tr>
<td>4</td>
<td>0.04</td>
<td>4.06 e-3</td>
<td>1.3 e-7</td>
</tr>
</tbody>
</table>

Carbon Steel Electrode for \( w/o \text{H}_2\text{O}_2 \) - Pitting Factor = 11.3

3.3.3 Current Analysis

The current traces for these runs are shown in Figure 3.8. There is no significant difference in either the mean current or the standard deviation for the two runs. The mean value, standard deviation and area under each curve are listed in Table 3.5.

Table 3.5. Current Analysis for Simulated Radiation Comparison Runs

<table>
<thead>
<tr>
<th>Run Description</th>
<th>Mean Current Value (A)</th>
<th>Standard Deviation (A)</th>
<th>Area Under Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w/ \text{H}_2\text{O}_2 )</td>
<td>-4.06 e-5</td>
<td>6.99 e-5</td>
<td>1.16</td>
</tr>
<tr>
<td>( w/o \text{H}_2\text{O}_2 )</td>
<td>4.96 e-6</td>
<td>7.48 e-5</td>
<td>1.09</td>
</tr>
</tbody>
</table>

The power spectrums for the simulated radiation comparisons are shown in Figure 3.9. The psd curves show no noticeable effect from the addition of one ppm hydrogen peroxide.
3.4 Different Metals Comparison

3.4.1 Experimental Parameters

Tests were completed with the test materials - cast iron, carbon steel, and titanium - and their corrosion activity was compared. All runs were completed at 90°C for 24 hours with no peroxide additions or irradiation.

3.4.2 Pitting Analysis

Microscopy pictures and calculational layers are shown for the cast iron electrode in Appendix B and C, respectively. The carbon steel electrode layers are also shown in Appendix C with corrosion analysis data presented in Table 3.2. Titanium did not pit but before and after testing pictures were shown in Figures 3.4 and 3.5. Table 3.6 lists the percentage of area corroded, the average depth, and an estimated corroded volume for each cast iron electrode layer. The pitting factor determined from the deepest pit is also given.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Percentage of Area Corroded</th>
<th>Average Layer Depth (in)</th>
<th>Estimated Volume Corroded (in$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast Iron Electrode</td>
<td>-</td>
<td>Pitting Factor = 2.25</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>13.69</td>
<td>8.8 e-4</td>
<td>2.3 e-5</td>
</tr>
<tr>
<td>2</td>
<td>2.16</td>
<td>1.44 e-3</td>
<td>2.7 e-6</td>
</tr>
<tr>
<td>3</td>
<td>0.04</td>
<td>1.98 e-3</td>
<td>4.6 e-8</td>
</tr>
</tbody>
</table>

3.4.3 Current Analysis

The current traces for these runs are shown in Figure 3.10. The area under the curve for the carbon steel electrode was three orders of magnitude greater than for either of the others. Carbon steel also had the highest mean value and standard deviation. The titanium sample and the cast iron sample had similar mean values, but the cast iron electrode had a greater standard deviation. The cast iron electrode experienced two large current spikes and two smaller, but still noticeable, spikes. The carbon steel current trace showed spikes but they had an exponential decay rather than the sharp return to the normal value of the cast iron trace. The titanium current trace had activity in the first hour, probably from heatup, and then was essentially flat. The mean value, standard deviation and area under each curve are listed in Table 3.7.
Figure 3.8. Current Data for Simulated Irradiation Comparison

Figure 3.9. Power Spectrums for Simulated Irradiation Comparison
Table 3.7. Current Analysis for Different Metals Comparison Runs

<table>
<thead>
<tr>
<th>Run Description</th>
<th>Mean Current Value (A)</th>
<th>Standard Deviation (A)</th>
<th>Area Under Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast Iron</td>
<td>4.61 e-7</td>
<td>1.35 e-6</td>
<td>8.88 e-3</td>
</tr>
<tr>
<td>Carbon Steel</td>
<td>7.02 e-5</td>
<td>2.71 e-5</td>
<td>1.40</td>
</tr>
<tr>
<td>Titanium</td>
<td>7.17 e-8</td>
<td>4.48 e-8</td>
<td>1.43 e-3</td>
</tr>
</tbody>
</table>

The power spectrums for the simulated radiation comparisons are shown in Figure 3.11. As could be predicted from the current data, the power spectrum for the carbon steel sample is the highest - indicating the greatest corrosion activity. The titanium spectrum is the lowest, and the cast iron spectrum is in-between the others. The cast iron and titanium spectrums have the same general shape, but the carbon steel trace is noisier and has a steeper slope.

3.5 Loading Geometry

The Conax fitting at the top of the inner can has six ports for instrumentation. Three are used for electrode wires and one for the thermocouple, leaving two available for future options. The loading geometry for all tests are listed in Tables 3.8-11. The abbreviations used in these tables are TC = thermocouple, RE = reference electrode, CS = carbon steel, CI = cast iron, Inc = Inconel and Ti = titanium.

Table 3.8. Loading Data for Temperature Comparison Runs

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Position in Conax Fitting</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C</td>
<td>blank, TC, blank, Inc#8, RE, CS#1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50°C</td>
<td>blank, TC, blank, CS#2, RE, Inc#7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25°C</td>
<td>blank, TC, blank, Inc#7, RE, CS#3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.9. Loading Data for Radiation Comparison Runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Position in Conax Fitting</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>in lab</td>
<td>blank, TC, blank, Ti#5, RE, Ti#6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in SFP</td>
<td>blank, TC, blank, Ti#8, RE, Ti#7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.10. Current Data for Different Metals Comparisons
(CI and Ti are on the right axis, CS is on the left axis)

Figure 3.11. Power Spectrums for Different Metals Comparisons
### Table 3.10. Loading Data for Simulated Radiation Comparison Runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Position in Conax Fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>w/ H₂O₂</td>
<td>blank</td>
</tr>
<tr>
<td>w/o H₂O₂</td>
<td>blank</td>
</tr>
</tbody>
</table>

### Table 3.11. Loading Data for Different Metals Comparison Runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Position in Conax Fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>Cl</td>
<td>blank</td>
</tr>
<tr>
<td>CS</td>
<td>blank</td>
</tr>
<tr>
<td>Ti</td>
<td>blank</td>
</tr>
</tbody>
</table>
4 Discussion and Conclusions

The results from the previous chapter are discussed here. Section 4.1 develops correlations between total corroded volume, pitting factor, area under the current trace and slope of the psd for the temperature comparison electrodes. Section 4.2 discusses the electrochemical noise analysis from the radiation comparisons, but no correlations are possible for lack of physical corrosion results for the titanium electrodes. Section 4.3 presents discussion on the simulated irradiation tests, and Section 4.4 compares the qualities of cast iron, carbon steel and titanium electrodes. Section 4.5 provides conclusions about the analysis results.

4.1 Temperature Comparisons

The corrosion data for the electrodes used in the temperature comparisons are shown in Table 3.2. The percentage of area corroded and the estimated total corroded pitting volume versus the layer number are indicated graphically in Figures 4.1 and 4.2. The electrode used for the 90°C tests experienced the most localized corrosion activity as evidenced by the greatest pit depth of 5.74 e-3 inches and the largest total pitting volume corroded of 1.09 e-5 cubic inches.

The pitting factor, determined from the deepest pit, was evaluated for use as a parameter for comparison of electrode performance. The total estimated volume corroded was also measured because it accounts for the percentage of area corroded on each layer as well as the layer depth. The volume of the first layer is considered uniformly corroded volume and is not included in the total pitting volume. The pitting factor and the total pitting volume corroded are listed for each electrode in Table 4.1. Unfortunately, a relationship between significant spikes on the current trace and differentiable pitting areas on the electrode was not apparent. The 90°C test had four large definite spikes as well as many smaller ones; but the electrode surface showed hundreds of pits in line-like patterns that did not evolve at deeper layers into specific regions of identifiable pit initiation sites.

It is desirable to correlate the physical corrosion data with the electrochemical information obtained in the current analysis. The area under each current trace is listed in Table 3.3 and is shown again in Table 4.1. The pitting factor, estimated pitting volume and area under the current trace all
Figure 4.1. Corroded Area for Temperature Comparison Electrodes

Figure 4.2. Corroded Volume for Temperature Comparison Electrodes
trend in the expected direction, indicating most corrosion activity on the 90°C test electrode. The psd curves are most useful for graphical comparisons. For a psd line equation, the best curve fit is a fifth order polynomial with the coefficients shown in Table 4.2 for x values from 3.125e-5 to 2.5e-1. The equation is of the form \( y = M_0 + M_1(x) + M_2(x^2) + M_3(x^3) + M_4(x^4) + M_5(x^5) \).

For a simpler but less accurate comparison in the region of the curve with x values from 3.125e-5 to 3.0e-3, a logarithmic curve fit of \( y = m(\log x) + b \) can be used to determine the slope of the lines as shown in Table 4.3. The slopes are essentially the same, and may be indicative of metal type rather than localized corrosion behavior.

Table 4.1. Analysis Results for Temperature Comparison Electrodes

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Pitting Factor</th>
<th>Total Estimated Volume Corroded</th>
<th>Area Under the Current Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C</td>
<td>5.52</td>
<td>1.09e-5 in³</td>
<td>1.40</td>
</tr>
<tr>
<td>50°C</td>
<td>1.95</td>
<td>4.77e-6 in³</td>
<td>1.33</td>
</tr>
<tr>
<td>25°C</td>
<td>1.49</td>
<td>2.57e-7 in³</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Table 4.2. Fifth Order Polynomial Curve Fit Coefficients

<table>
<thead>
<tr>
<th>Test</th>
<th>R²</th>
<th>M0</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C</td>
<td>0.68</td>
<td>-121</td>
<td>-1505</td>
<td>2.8e4</td>
<td>-2.4e5</td>
<td>9.2e5</td>
<td>-1.3e6</td>
</tr>
<tr>
<td>50°C</td>
<td>0.98</td>
<td>-144</td>
<td>-932</td>
<td>9.0e3</td>
<td>-4.3e4</td>
<td>8.8e4</td>
<td>-8.8e3</td>
</tr>
<tr>
<td>25°C</td>
<td>0.96</td>
<td>-155</td>
<td>-1066</td>
<td>-1.4e4</td>
<td>-7.6e4</td>
<td>1.6e5</td>
<td>-8.7e3</td>
</tr>
</tbody>
</table>

Table 4.3. Slope Values for Logarithmic Curve Fit

<table>
<thead>
<tr>
<th>Test Description</th>
<th>R² Value</th>
<th>Slope of PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°C</td>
<td>0.90</td>
<td>-14.89</td>
</tr>
<tr>
<td>50°C</td>
<td>0.94</td>
<td>-14.25</td>
</tr>
<tr>
<td>25°C</td>
<td>0.96</td>
<td>-15.35</td>
</tr>
</tbody>
</table>

4.2 Radiation Comparisons

Since the titanium electrodes experienced no measurable surface deformation, the pitting factor was not calculated. Deepest pit and total corroded volume information was also not available. Despite the lack of physical corrosion data, electrochemical noise analysis was possible. For a psd
line equation, the best curve fit is a fifth order polynomial with the coefficients shown in Table 4.4 for x values form 4.0e-5 to 5.0e-2. For a simpler but less accurate comparison in the region of the curve with x values from 4.0e-5 to 4.0e-3, a logarithmic curve fit of \( y = m \log(x) + b \) can be used to determine the slope of the lines as shown in Table 4.5. Once again, the slopes are essentially the same. However, the titanium psd slopes are about twice as large as the carbon steel psd slopes, supporting the theory of psd slopes indicating metal type rather than localized corrosion behavior. The area under the current traces for the titanium electrodes are several orders of magnitude lower than the carbon steel electrodes which supports the theory of a relationship between the area under the current trace and the total corroded volume, since the volumes for the titanium electrodes were negligible in these tests.

<table>
<thead>
<tr>
<th>Test</th>
<th>R²</th>
<th>M0</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>in lab</td>
<td>0.88</td>
<td>-183</td>
<td>-6596</td>
<td>-5.1e5</td>
<td>-1.9e7</td>
<td>3.1e8</td>
<td>-1.9e9</td>
</tr>
<tr>
<td>in SFP</td>
<td>0.67</td>
<td>-221</td>
<td>-3194</td>
<td>1.9e5</td>
<td>-3.4e6</td>
<td>-2.1e7</td>
<td>8.0e8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Description</th>
<th>R² Value</th>
<th>Slope of PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>in lab</td>
<td>0.94</td>
<td>-27.77</td>
</tr>
<tr>
<td>in SFP</td>
<td>0.93</td>
<td>-29.04</td>
</tr>
</tbody>
</table>

### 4.3 Simulated Irradiation Comparisons

The corrosion data for the electrodes used in the simulated radiation comparisons was shown in Table 3.7. The percentage of area corroded and the estimated pitting volume corroded versus the layer number are shown graphically in Figures 4.3 and 4.4. The electrode in the test without hydrogen peroxide added experienced somewhat greater total corroded pitting volume, although they are still within the same order of magnitude. The possible pit initiation sites on the microscopy surface pictures are somewhat more quantifiable, but again there is no obvious correlation with the current spikes.
Figure 4.3. Corroded Area for Simulated Irradiation Comparison Electrodes

Figure 4.4. Corroded Volume for Simulated Irradiation Comparison Electrode
from the electrochemical noise data. The pictures of the layers are shown in Appendix B.

The pitting factor and the total estimated volume corroded are listed for each electrode in Table 4.6 with the area under the current trace. These areas are very similar for both tests as expected from the current data in Figure 3.7. The pitting factors and the total corroded volumes are similar but higher in both cases for the electrode in the test without hydrogen peroxide added. For the psd curves, the best curve fit is a fifth order polynomial with the coefficients shown in Table 4.7 for x values from 6.0e-5 to 1.0e0. For a simpler but less accurate comparison in the region of the curve with x values from 6.0e-5 to 1.0e-2, a logarithmic curve fit of \( y = m(\log x) + b \) can be used to determine the slope of the lines as shown in Table 4.8. The psd slopes are very similar, and they are similar to the slopes of the psd curves for the temperature comparison electrodes which were also carbon steel.

Table 4.6. Analysis Results for Simulated Irradiation Comparison Electrodes

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Pitting Factor</th>
<th>Total Estimated Volume Corroded</th>
<th>Area Under the Current Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/ H₂O₂</td>
<td>8.12</td>
<td>1.9 e-6 in³</td>
<td>1.16</td>
</tr>
<tr>
<td>w/o H₂O₂</td>
<td>11.3</td>
<td>7.1 e-6 in³</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Table 4.7. Fifth Order Polynomial Curve Fit Coefficients

<table>
<thead>
<tr>
<th>Test</th>
<th>R²</th>
<th>M0</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/ H₂O₂</td>
<td>0.82</td>
<td>-141</td>
<td>-90.9</td>
<td>126</td>
<td>88.5</td>
<td>-323</td>
<td>201</td>
</tr>
<tr>
<td>w/o H₂O₂</td>
<td>0.87</td>
<td>-143</td>
<td>-69.6</td>
<td>-76.2</td>
<td>642</td>
<td>-920</td>
<td>422</td>
</tr>
</tbody>
</table>

Table 4.8. Slope Values for Logarithmic Curve Fit

<table>
<thead>
<tr>
<th>Test Description</th>
<th>R² Value</th>
<th>Slope of PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/ H₂O₂</td>
<td>0.97</td>
<td>-18.66</td>
</tr>
<tr>
<td>w/o H₂O₂</td>
<td>0.97</td>
<td>-17.11</td>
</tr>
</tbody>
</table>
4.4 Different Metals Comparisons

The corrosion data for the carbon steel and cast iron electrodes used in the simulated radiation comparisons is shown in Tables 3.2 and 3.10. Titanium did not experience localized corrosion so it was not included in the corrosion analysis; Polaroid® pictures of the surface before and after testing were shown in Figures 3.3 and 3.4. The microscopy pictures for the cast iron layers are shown in Appendix B. The percentage of area corroded and the estimated pitting volume corroded versus the layer number are shown graphically in Figures 4.5 and 4.6. The uniformly corroded depth was greater than for the carbon steel electrodes, and the pits underneath were predominantly found at the boundaries of the epoxy insulation. The pit structure did not correspond to the four distinct current spikes.

The pitting factor and the total estimated volume corroded are listed for the carbon steel and cast iron electrodes in Table 4.9 with the area under the current traces. The cast iron electrode has a lower pitting factor than the carbon steel electrode, primarily because the cast iron electrode had deeper uniform corrosion. After removal of the top layer, the cast iron did have very deep pits as did the carbon steel but not as many. The total estimated corroded volume was also much lower for the cast iron. The area under the cast iron current trace was orders of magnitude lower than for carbon steel; the areas for cast iron and titanium were similar.

For the psd curves, the best fit is a fifth order polynomial with the coefficients shown in Table 4.7 for x values from 3.1e-5 to 2.5e-1. For a simpler but less accurate comparison in the region of the curve with x values from 3.1e-5 to 1.0e-2, a logarithmic curve fit of $y = m(log x) + b$ can be used to determine the slope of the lines as shown in Table 4.8. The cast iron slope was between the carbon steel and titanium slopes, but closer to the value for titanium.

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Pitting Factor</th>
<th>Total Estimated Volume Corroded</th>
<th>Area Under the Current Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI</td>
<td>2.25</td>
<td>2.7 e-6 in³</td>
<td>8.88 e-3</td>
</tr>
<tr>
<td>CS</td>
<td>5.52</td>
<td>1.1 e-5 in³</td>
<td>1.40</td>
</tr>
<tr>
<td>Ti</td>
<td>n/a</td>
<td>n/a</td>
<td>1.43 e-3</td>
</tr>
</tbody>
</table>
Figure 4.5. Corroded Area for Different Metals Comparison Electrodes

Figure 4.6. Corroded Volume for Different Metals Comparison Electrodes
Table 4.10. Fifth Order Polynomial Curve Fit Coefficients

<table>
<thead>
<tr>
<th>Test</th>
<th>R²</th>
<th>M0</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI</td>
<td>0.86</td>
<td>-153</td>
<td>-1050</td>
<td>1.5 e4</td>
<td>-8.8 e4</td>
<td>2.1 e5</td>
<td>-1.1 e5</td>
</tr>
<tr>
<td>CS</td>
<td>0.68</td>
<td>-121</td>
<td>-1505</td>
<td>2.8 e4</td>
<td>-2.4 e5</td>
<td>9.2 e5</td>
<td>-1.3 e6</td>
</tr>
<tr>
<td>Ti</td>
<td>0.88</td>
<td>-183</td>
<td>-6596</td>
<td>-5.1 e5</td>
<td>-1.9 e7</td>
<td>3.1 e8</td>
<td>-1.9 e9</td>
</tr>
</tbody>
</table>

Table 4.11. Slope Values for Logarithmic Curve Fit

<table>
<thead>
<tr>
<th>Test Description</th>
<th>R² Value</th>
<th>Slope of PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI</td>
<td>0.89</td>
<td>-24.96</td>
</tr>
<tr>
<td>CS</td>
<td>0.90</td>
<td>-14.89</td>
</tr>
<tr>
<td>Ti</td>
<td>0.94</td>
<td>-27.77</td>
</tr>
</tbody>
</table>

4.5 Conclusions of Analysis Results

Localized corrosion activity was greater for carbon steel at higher temperatures. The pitting factor, estimated total pitting volume and area under the current curve calculations for the temperature comparisons all trend in the correct direction to verify these results. The logarithmic curve fit slopes for the carbon steel electrodes were all very similar. There was no apparent relationship between spikes on the current trace and physical surface analysis for either carbon steel or cast iron.

Titanium experienced no measurable surface deformation so corrosion analysis results were not available. The logarithmic curve fit slopes were similar, but substantially different than the slopes for the carbon steel electrodes. The area under the current trace for titanium was orders of magnitude less than for carbon steel, and the estimated total corroded volume was negligible for the titanium samples.

Simulated irradiation by one ppm H₂O₂ produced no significant change in the electrochemical noise analysis results, although the physical corrosion analysis showed slightly more localized corrosion on the carbon steel electrode in the test without added H₂O₂. The logarithmic curve fit slopes were similar and close to the slopes for the carbon steel electrodes.

The cast iron samples had greater uniform corrosion than any of the other electrodes. The calculated areas under the current trace were similar for the cast iron and titanium samples, and the total estimated corroded volume for cast iron was much lower than for carbon steel.
5 Conclusions

5.1 Method as a Predictive Tool

The slope of the logarithmic curve fit of the psd may be indicative of the metal type. For carbon steel, these slopes are lowest and range from 14.25 to 18.66. The titanium slopes were highest, ranging from 27.77 to 29.04, and the slope of the cast iron sample was 24.96. More test runs completed for each metal type could verify the reliability of the slope as a predictive tool.

The area under the current curve may be indicative of the total estimated corroded volume. This is very useful for two reasons. First, this relationship shows a correlation between the electrochemical noise data and the physical corrosion analysis, proving this technique as a meaningful tool. Second, this has important implications for passive monitoring of waste canisters because analysis of the electrochemical noise data aboveground could be used to predict with some confidence the remaining lifetime of the canisters underground.

Since the pitting factor accounts for both uniform corrosion and greatest pit depth, it should be possible to predict when a waste canister will be breached from pitting factor analysis. Some refinement of the pitting factor calculation is necessary to ensure the reliability of this method.

5.2 Experimental Apparatus

Sample preparation could be improved upon. The surface area was difficult to precisely reproduce after cutting, polishing and insulating the electrodes. The polishing procedure could be made easier by automation of the sanding stages. Attachment of the instrument wires worked well since soldering avoided the heat treatment that would have occurred with brazing or welding.

The experimental setup performed well. Full heatup of the inner can was accomplished quickly, and temperature control was very good. Pressure monitoring was operable and is available for future test runs at temperatures above boiling. Water flow was measured but not well-controlled, probably because the water was siphoned through the assembly. A slow pumping unit might have been a better choice for the flow system. Assembly and disassembly of the inner can was simple, and the frame inside the can provided reproducible alignment of the electrodes.
5.3 Analysis Techniques

LabVIEW® proved to be a valuable tool, easily accomplishing data acquisition, storage, analysis and transfer. It was relatively simple to program and interfaced well with a wide variety of instruments. The microscopy pictures were useful too, although inputting data from them for the corrosion analysis relied on manual tracing. The possible error is expected to be in the total corroded volume calculation which depends on the surface area of the electrode, the percentage of area corroded and the layer depth. The surface area is reasonably well-defined, but the layer depth is averaged from five points on the electrode surface so there could be variations in this calculation. The percentage of area corroded is calculated by AutoCAD® from the microscopy pictures and depends on accurate tracing of surface deformities.
6 Future Work

Continued study in this area is needed to provide a more fundamental understanding of the results which have been obtained. Increased temperature has been shown to increase the localized corrosion of active metals such as carbon steel, and substantial radiation decreased the localized corrosion activity of stable metals such as titanium. A larger number of test runs is necessary to decrease statistical errors and verify these results. Reproducible methods in sample preparation, including surface polishing and epoxy insulation, will produce less surface defects and surface area variation among electrodes.

The errors in the corrosion analysis procedure need to be reduced before this information can be used as more than an order of magnitude approximation. The pitting factor and total corroded volume are very useful parameters and could provide further understanding and verification of the electrochemical noise data.

With the use of fiber optics for in-situ monitoring of the chemistry at the surface of the electrodes, more information can be obtained about the mechanisms involved. Changes in pH at the electrode surface during the onset of pitting can be determined as can concentrations of hydrogen peroxide and other species. The two extra ports in the Conax fitting can be used for fiber optics entering and leaving the inner can. The information obtained from in-situ monitoring of the electrode surface chemistry will provide more fundamental understanding of the localized corrosion mechanisms and the effects of radiation on them.
REFERENCES


APPENDIX A

The front panels and the block diagrams for the LabVIEW® VI's used in data acquisition and analysis are shown and discussed here. The standard machine interface VI's to write and read messages, open and close instruments, check errors, etc. are not included. For block diagrams, all main sequences and some decision loops are shown. Since a false value merely results in an error message in many cases, most boolean loops only show the true case. A brief discussion on the logic flow is also included for each VI.
To pass information between the voltmeter and LabVIEW®, the voltmeter is first initialized. This verifies the GPIB address which has been set manually from the instrument front panel and sets up the functions for remote access and control. For multiple instruments, the identification number is important to ensure correct communication and eliminate bus errors. If either the GPIB address or instrument identification number does not match the voltmeter, an error will occur. The error shown on the front panel gives the user information about its cause. Other communications problems or stale data will also cause errors which are listed in the voltmeter user manual. The initialization front panel is shown in Figure A.1.

In the block diagram, the GPIB address opens the correct instrument and returns the instrument identification number. This number is sent back to query the instrument and perform error checking. If the query does not return the correct response, an error is set and the instrument is closed. The last step checks the event status for the proper execution of the previous steps. An error will result if any one of these steps does not function correctly. If the initialization is successful, the instrument front panel will show the commands INIT and REM. Then the instrument will only be operable remotely from the LabVIEW® front panel. The block diagram sequences for the voltmeter initialization VI are shown in Figures A.2-5.

Figure A.1. Front Panel for Voltmeter Initialization VI
Enter instrument into Instrument Table and initialize global error variable.

Figure A.2. Block Diagram Sequence 1 for Voltmeter Initialization VI

Perform instrument identification query.

Figure A.3. Block Diagram Sequence 2 for Voltmeter Initialization VI
Figure A.4. Block Diagram Sequence 3 for Voltmeter Initialization VI

Figure A.5. Block Diagram Sequence 4 for Voltmeter Initialization VI
The front panel for the voltmeter VI resembles the actual instrument front panel. Remote operation of the voltmeter is only possible while the initialization VI for the voltmeter is also open. The voltmeter can be initialized from the front panel by using the initialize button with the correct instrument identification number. This should not be used while the VI is in continuous operation mode because attempting to initialize when the voltmeter is already showing the INIT command results in a stale data error. A sliding selector switch is used to choose the function with the options being period, frequency, 4-wire Ω, 2-wire Ω, current DC, current AC, voltage ratio, voltage DC and voltage AC. For these experiments, the voltage DC function was used. A sliding selector switch is also used to choose resolution. Speed is determined by resolution with 4 1/2 digits being the fastest pre-programmed option, with up to 1000 readings per second. The range can either be specified by the numeric control or by adjusting the autorange on/off switch. The user specifies the instrument delay in milliseconds, allowing continuous data acquisition when set to zero. The instrument measurement is sent to the output display and is also shown on the voltage stripchart. Data trends can be viewed during operation by changing the y-axis values or by adjusting the scroll bar on the x-axis. The front panel for the voltmeter operation VI is shown in Figure A.6.

The first function of the block diagram is initialization of the voltmeter if required. Then the instrument waits the specified delay time from the user input on the front panel and clears the global error variable by setting the error buffer of the voltmeter to zero. The resolution, function and range commands from the front panel are formatted and written to the instrument. The measurement can then be read and the error message is scanned. If no error has occurred in formatting, writing and reading, the buffer value will still be zero and the measurement will be considered valid. The error and measurement output readings are then updated. The final step is checking the status byte of the voltmeter for correct operation of all the above steps. If an error does occur in this final step, the measurement value cannot be considered valid although it was updated. These block diagram sequences for the voltmeter operation VI are shown in Figures A.7-13.
Front Panel

**Figure A.6. Front Panel for Voltage Operation VI**

Block Diagram

**Figure A.7. Block Diagram Sequence 1 for Voltage Operation VI**
Figure A.8. Block Diagram Sequence 2 for Voltage Operation VI

Figure A.9. Block Diagram Sequence 3 for Voltage Operation VI
Figure A.10. Block Diagram Sequence 4 for Voltage Operation VI

Figure A.11. Block Diagram Sequence 5 for Voltage Operation VI
Figure A.12. Block Diagram Sequence 6 for Voltage Operation VI

Figure A.13. Block Diagram Sequence 7 for Voltage Operation VI
The picoammeter does not require a separate initialization VI as does the voltmeter but otherwise, its concept of operation is very similar. The functions for the picoammeter include range, log, relative operation and trigger. Range, trigger and relative operation are controlled with sliding selector switches, and the settings used for these experiments were auto range, continuous trigger and relative off. Log uses an on/off switch with the default position being off. The user specifies the instrument delay in milliseconds, allowing continuous data acquisition when set to zero. The instrument measurement is sent to the output display and is also shown on the current stripchart. Data trends can be viewed during operation by changing the y-axis values or by adjusting the scroll bar on the x-axis. The front panel for the current operation VI is shown in Figure A.14.

The block diagram starts with the user-specified delay indicated on the front panel. Then the function settings are formatted to a command string and sent to the instrument. A very short delay of ten ticks is also included to allow for picoammeter setup time. The data is returned from the instrument as a string and converted to a number with certain directions for out-of-range readings. The picoammeter VI involves much less error checking than the voltmeter VI. This allows the picoammeter to operate slightly faster than the voltmeter and can be accounted for by adjusting the picoammeter setup time in the third sequence. Reduced error checking could also result in less reliable data, but the picoammeter usually considers bad data as an out-of-range measurement after converting it from a string to a number. The block diagram sequences for the current operation VI are shown in Figures A.15-18.
Figure A.14. Front Panel for Picoammeter Operation VI
Figure A.15. Block Diagram Sequence 1 for Picoammeter Operation VI

Figure A.16. Block Diagram Sequence 2 for Picoammeter Operation VI
Figure A.17. Block Diagram Sequence 3 for Picoammeter Operation VI

DELAY - ALLOW FOR METER SETUP TIME.

Figure A.18. Block Diagram Sequence 4 for Picoammeter Operation VI

READ BACK DATA FROM 485, CONVERT STRING TO A NUMBER, RETURN 9.9E9 ON OVER RANGE, -9.9E9 ON NEGATIVE OVER RANGE.
Data acquisition is accomplished by accessing both the voltmeter and the picoammeter. The front panel provides an on/off button to allow the user to disable one of the instruments. The user also specifies the delay in milliseconds, allowing continuous data acquisition when set to zero. The instrument measurement is sent to the output displays and also shows on the voltage and current stripcharts. Data trends can be viewed during operation by changing the y-axis values or by adjusting the scroll bar on the x-axis. The front panel for the data acquisition VI is shown in Figure A.19.

The block diagram has conditional true/false boxes controlled by the value of the on/off buttons of the front panel for the voltmeter and the picoammeter. The value of the delay is sent to the voltmeter or picoammeter operational VI which returns the measurement value. This is sent to the output numerical display and the voltage or current graphical display. The block diagram for the data acquisition VI is shown in Figure A.20.

Figure A.19. Front Panel for Data Acquisition VI
Figure A.20. Block Diagram for Data Acquisition VI
The data analysis VI provides statistical information and performs the power spectral density calculations. The user specifies the first and last run numbers to be accessed from the data acquisition VI, and the current trace from this selected data segment is redrawn on the current x-y graph. The data points are also sent to a two-dimensional array available from the front panel. The power spectral density is calculated for the current trace and output numerically to a two-dimensional array and graphically to the spectral density x-y graph. The voltage measurements from the selected data segment are also accessed (but not sent to an array), and the mean and standard deviation are output to the front panel for both the current and voltage traces. If any problem occurs in accessing the data acquisition VI or transferring measurements, the error button changes color. The comment box allows the user to record important test parameters such as date, temperature, materials and radiation history for the run being analyzed. The front panel for the data analysis VI is shown in Figure A.21.

The block diagram uses only one sequence, and a for loop accesses each data point. The difference between the user-specified first and last run numbers is sent to the for loop to indicate the required number of iterations. Once inside the for loop, the data acquisition VI is treated as a data base. The logged data file corresponding to the sum of the first run number and the i value of the for loop is accessed and separated into clusters representing the output variables on the front panel of the data acquisition VI. The data base control also sends an error message if necessary. From the data base clusters, the voltage and current data points leave the for loop to become arrays. These arrays are input to the statistical analysis subVI that returns their mean and standard deviation to the front panel. The current array is also sent as output to the front panel, and it is input to the power spectrum analysis subVI. After the power spectrum calculations, the output array is wired to a log conversion VI and multiplied by ten, resulting in decibel units for the psd array that is sent to the front panel. The psd array is also input as the y axis to the spectral density graph on the front panel. The x axis array is calculated by accessing the delay from the data acquisition VI, converting it to seconds by dividing by 1000, multiplying by the total number of points in the selected data segment and inverting the final result. The last step is to update the comment box on the front panel with user-specified input. The block diagram for the data analysis VI is shown in Figure A.22.
Figure A.21. Front Panel for Data Analysis VI

Figure A.22. Block Diagram for Data Analysis VI
The data transfer VI sends clusters of information to spreadsheet files outside LabVIEW® to enable graphing or data manipulation by other software programs. The front panel allows the user to specify the source file path in the volume:folder:file string control with the default being selected by dialog window. The output file path is chosen by the volume:folder:file string indicator again selected by dialog window. If the file selection process is canceled, this indicator will be blank. The output data is sent to the file as a string formatted in the standard C language style and controlled by the user from the front panel. Control inputs are also provided on the front panel to allow the user to select the number of data points to be transferred and the logged data number from the data analysis VI. The error button will change color upon any input or output file malfunctions, an invalid run number or sample number or an incorrectly formatted output string. The file error box on the front panel will give numeric indication of the specific error that has occurred. The front panel for the data transfer VI is shown in Figure A.23.

The block diagram for the data transfer VI begins by accessing the data analysis VI database with the logged run number from the front panel. An error will result if necessary. The array of current values is input to a for loop where they are averaged in groups of ten data points. The sample number value from the front panel is divided by ten and sent to the for loop to determine the number of iterations. The current array is separated by accessing a segment of size ten beginning at the i value of the for loop multiplied by ten. The summation of this segment is then divided by ten and sent out of the for loop as an averaged array into the conditional true/false box to be formatted and transferred. Meanwhile, the source file is selected and sent to another conditional true/false box with a true value if the source file exists. Inside the conditional box, a dialog window is opened to allow the user to select an output file, and this file name is shown in the string indicator on the front panel. If the file does not already exist, a new file with the chosen name is opened. A conditional value from this true/false box is sent to the format and transfer box. Errors in the path name, content of the file or opening new file subVI will result in a false value being passed. If a true value is passed, the averaged current value is formatted in the manner indicated on the front panel and transferred to the output file. This file is then closed and any errors are sent to the front panel. The block diagram for the data transfer VI is shown in Figure A.24.
Front Panel

Figure A.23. Front Panel for Data Transfer VI

Block Diagram

Figure A.24. Block Diagram for Data Transfer VI
APPENDIX B

The microscopy pictures reproduced here are representative of the layer photos used in corrosion analysis with an 8X magnification. All of the temperature comparison electrode layer pictures are shown, as are all of the cast iron layers. Several of the layers from the simulated irradiation comparison runs are also included.
Figure B.1. Layer #1 (Top Layer) for 90°C Test Carbon Steel Electrode

Figure B.2. Layer #2 for 90°C Carbon Steel Electrode
Figure B.3. Layer #3 for 90°C Carbon Steel Electrode

Figure B.4. Layer #4 for 90°C Carbon Steel Electrode
Figure B.5. Layer #5 (Bottom Layer) for 90°C Carbon Steel Electrode

Figure B.6. Layer #1 (Top Layer) for 50°C Carbon Steel Electrode
Figure B.7. Layer #2 for 50°C Carbon Steel Electrode

Figure B.8. Layer #3 for 50°C Carbon Steel Electrode
Figure B.9. Layer #4 (Bottom Layer) for 50°C Carbon Steel Electrode

Figure B.10. Layer #1 (Top Layer) for 25°C Carbon Steel Electrode
Figure B.11. Layer #2 for 25°C Carbon Steel Electrode

Figure B.12. Layer #3 (Bottom Layer) for 25°C Carbon Steel Electrode
Figure B.13. Layer #1 for Simulated Irradiation Test with H$_2$O$_2$ Added

Figure B.14. Layer #2 for Simulated Irradiation Test without H$_2$O$_2$ Added
Figure B.15. Layer #1 (Top Layer) for Cast Iron Electrode

Figure B.16. Layer #2 for Cast Iron Electrode
Figure B.17. Layer #3 (Bottom Layer) for Cast Iron Electrode
APPENDIX C

The AutoCAD® pictures shown here were used for percentage of area corroded calculations. They were manually traced with an ADB® digitizer and the area of the polygons was estimated with the Advanced Modeling Extension®. The polygons on the layers represent the corroded surface on the electrodes and are shown here with two-directional hatching in order to differentiate between the layers when seen from an overhead viewpoint.
Figure C.1. Corroded Surface Representation of 90°C Test Electrode
Figure C.2. Corroded Surface Representation of 50°C Test Electrode
Figure C.3. Corroded Surface Representation of 25°C Test Electrode
Figure C.4. Corroded Surface Representation of Simulated Irradiation Test with $\text{H}_2\text{O}_2$ Added
Figure C.5. Corroded Surface Representation of Simulated Irradiation Test without $\text{H}_2\text{O}_2$ Added
Figure C.6. Corroded Surface Representation of Cast Iron Electrode