Innovative Approach to SCC Inspection and Evaluation of Canister in Dry Storage

Integrated Research Project

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Final Report

Innovative Approach to SCC Inspection and Evaluation of Canister in Dry Storage


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This final report is summarized four years of work of awarded project number DE-NE0008442IRP-15-9318, title as: “Innovative Approach to SCC Inspection and Evaluation of Canister in Dry” supported by Nuclear Energy University Program/Integrated Research Program, NEUP/IRP, where last year is an extension of no cost project. This research work is focused on the possible degradation of dry storage canister holding used nuclear fuel (UNF), due to exposure of marine atmospheric environment. The canister usually designed from a welded austenitic stainless-steel of types 304 or 316, encased in a concrete shell known as an overpack. This canister designed and licensed for 20 years with an extension period need to be determined, in addition 20 years or more. These casks are located throughout the country in Independent Spent Fuel Storage Installations (IFSFIs) often on the site close to nuclear power plants, that are often located in coastal or lake-side regions where a marine atmospheric salt air environment exist. As a result of several recent decisions, such as not pursuing Yucca Mountain as a long-term geologic repository storage facility for UNF and the cancellation of the construction of a reprocessing facility in the 1980s due to proliferation risks, interim dry storage facilities for long-term storage are vital option for the immediate future of nuclear energy technology.

One of the primary concerns with respect to the long-term performance of the storage casks is the potential for corrosion initiation due to deliquescence of salts deposited on the canister surface as aerosols; in regions of high residual weld stresses, this may lead to localized stress corrosion cracking (SCC). Dust and aerosols in the air being drawn though ventilation openings in the overpacks of passively ventilated dry canister storage systems may be deposited on the stainless-steel canister outer surfaces. Under these conditions, localized corrosion attack can occur. Chlorides ions deliquescence on the canister surface, a process by which the salts essentially pull moisture out of the air, creating a concentrated salt brine on the canister surface. Chloride-induced stress corrosion cracking (CISCC) of welded zones is of special concern, as it a well-documented mode of attack for austenitic stainless steels marine environments, and many independent spent fuel storage installations (ISFSIs) are located in coastal areas. Recent canister inspections have shown that chloride salts are present on the surface of in-service canisters at near-marine settings. However, canister surface inspections of satisfactory resolution to detect SCC have never been carried out in details, because access to the canister surfaces through vents in the overpacks is extremely limited, and high radiation fields make removal of the canisters from the overpacks undesirable.

Although no significant corrosion damage has not been detected up to date, there is concern that this may lead to pitting corrosion, which could in turn develop into stress corrosion cracking, causing canister structural failure. The initiation and propagation of pitting corrosion has been widely studied in full immersion conditions, but limited studies have been done on marine atmospheric conditions, which is a focus of this work, these includes laboratory and field experimentally and propagation rate modeling of pitting and transition to crack, and crack propagation rate. It is known, however, that the rate of atmospheric corrosion can be affected by
variations in relative humidity (RH), salt density, salt type, droplet area, temperature and stainless-steel microstructure and residual stress particularly in welded zones of canisters. The integrated research program has identified potential deterioration mechanisms for the stainless-steel canisters containing the UNF in dry storage that require detailed research and investigation and will have an impact on the performance of long-term interim storage under the normal and extreme environmental conditions experienced during the duration of this storage. The prediction and monitoring of canister corrosion processes while in storage can provide important data for the assessment of interim storage performance and the safety to the public.

This report comprises of mainly the published results in different journals and covering a wide range spectrum from susceptible stainless-steel types 304\316 microstructural analysis through the implant test at atmospheric environment, residual stress analysis of mockup canister and simulation, inspection methodology includes nonlinear ultrasound and vibro-thermography and stochastic modeling and simulation of pits propagation rates and transition to cracks. Description of field specimens installed at ISFSI of Main Yankee is given in the following chapters and will be analyzed in the coming future and serves as an important data for a stochastic analysis as it was drawn from the publications and reports described in this report. The purpose of this report is to bring together the project efforts that includes improving in our understanding of structural aging performance at current dry storage casks fleet at ISFSIs in the context of remedial maintenance and inspection applications technologies.

This report is structured as follows:

- **Chapter 1**: Present an overview of the organized research program as it was represented in Materials Science and Technology conference in October 2016, titled as “Integrated Research Program Overview on the Innovative Approaches to Marine Atmospheric Stress Corrosion Cracking Inspection, Evaluation and Modeling in Used-fuel Dry Storage Canisters”, MS&T16, Transaction, Salt Lake City, UT, October 23-27, 2016 (14 pages). Additionally. It is also published in Advances in Materials Science for Environmental and Energy Technologies, transaction book, 2017, Wiley publications.

- **Chapter 2**: Described the data-based development process that used during project and includes enormous of published papers related to the project, external and internal reports, and experimental laboratory data internally and externally on pitting and stress corrosion crack propagation rate.

- **Chapter 3**: In this chapter a final report is given that summarized of an effort of understanding the impact of changing the microstructure of stainless-steel types 304 in controlled marine atmospheric environment on the boosting of development of pitting corrosion and cracks. This report titled as “Identification of Sensitized Microstructures in Welds in Spent Nuclear Fuel Containers Using the Controlled Environment Modified Implant Testing Technique”.


Chapter 4: Depicted total numbers of large 4-point bend specimens, and small size 4-pint specimens were loaded at Colorado School of Mines humidity chambers with maximum stress of 250MPa., and temperature of 50˚C, with relative humidity (RH) of 35% and 55% at early August 2017. In addition, 24 small 4-point bend specimens and 8 large 4-point bend specimens of stainless-steel, were placed at Maine Yankee for field test. These includes polished and unpolished specimens, to examine the impact of polish stainless-steel on pitting initiation rates. Description of the procedure prior to the actual installation and actual installation specimens work at Maine Yankee is also given in this chapter.

Chapter 5: Described the work performed at CSM in simulating residual stress\strain of canister mockup with ABAQUS software. The calculated residual stresses compared with the experimental measurements using deep-hole drilling (DHD) and contour methods provided by the collaborator project Sandia National Laboratories (SNL). The analysis includes Digital Image Correlation (DIC) method of images strain contours during incremental loading on the four points bends specimens made at Colorado school of mines loaded to humidity chambers and shipped to Sandia national laboratory and loaded into their atmospheric chamber’s humidity. The main goal of this work is to determine the impact of stress\strain on pitting\crack corrosion initiations and propagation rates at heat affected zone (HAZ) and on bulk surface. This report also includes the ABAQUS stress analysis on the pre-cracked specimens under different tensile loads in a corrosive environment to provide the stress and strain distributions around the crack tip. The report is titles as “Weld Residual Stress Analysis in the Canister Mockup”.

Chapter 6: Summarizes our preliminary analytical results for detecting small amount of chlorine using neutron activation analysis (NAA) and prompt gamma activation analysis (PGAA). The analysis is performed by MCNP6 computer code (well-known, multi-particle Monte Carlo simulation code). The goal was to determine the feasibility of using PGAA and NAA as an environmental inspection methodology for detecting and monitoring of small quantities of chlorine on canister surfaces that can be revealed on the outer surface of concrete overpack. The specific signature of gamma rays’ due reactions with sea salt constituents is documented and summarized in this report. An assessment of chloride presence at a canister surface is an essential before moving to other non-destructive analysis (NDA) methods for detection of pitting and cracking. Additionally, A paper was published at ANS winter meeting in November 2016 ANS at Las Vegas. Furthermore, it is also published in Advances in Materials Science for Environmental and Energy Technologies, transaction book, 2017 Volume VI, Wiley publications.

Chapter 7: Described the detection and monitoring capabilities that can be used for cracks finding on the surface of the canister the first part is focusing on application of Nonlinear Resonant Ultrasound Spectroscopy (NRUS) and the Time Reversed Elastic Nonlinearity Diagnostic (TREND) as it was proposed in the proposal. These efforts are performed at Brigham Young University (BYU) and summarized in three journal manuscripts. The first two manuscripts have been published in the journal of NDT&E International (comprising pages 3-
Chapter 8: The pitting and cracking corrosion evaluation projection is tightly integrated in our routine design of dry storage canisters, operational and maintenance for various dry storage casks structures at different IFSFIs. The two main components of pitting/cracking corrosion measurements exist one based on actual field data at IFSFIs sites and second on laboratory experiments under control environment, the correlation between them is not straightforward. These experiments data sets are the central of all mathematical models describing corrosion processes affecting structures. The lack of accuracy of corrosion forecasts can stem from two main types of factors. The first is the built-in uncertainty in the environment, material properties, and manufacturing process. The second is due to its chaotic character, that is, the fact that a small change can make significant impact on the results. Due to limited time of the project and unavailability of the data from the field this chapter is focused on the existing laboratory experimental data and are summarized in three published papers. The first one “An Application of Stochastic Modeling to Pitting of Spent Nuclear Fuel Canisters”, is published in Progress in Nuclear Energy. Volume 107, August 2018, Pages 48–56. [https://doi.org/10.1016/j.pnucene.2018.04.005](https://doi.org/10.1016/j.pnucene.2018.04.005). The stochastic method developed in this paper is applied to the reported of an experiment performed at Livermore National Laboratory. The second paper on “Modeling Pit Growth as a Function of Environmental Variables Through Stochastic Approaches,” is published in November 2018, Corrosion Journal of Science and Engineering: [DOI:10.5006/3017](https://doi.org/10.5006/3017). The third paper is on “Constructing and Application the Likelihood Function for Pits Growth Rates with Confidence Bounds”. Submitted to Corrosion Journal. This analysis is based on the experimental data from OSU where droplets of sea salt particles solutions are deposited on coupons surface of 304L and 316L stainless steels sheet to investigate the influence of different factors on the propagation and morphology of atmospheric corrosion pits. Key factors are the effect of residual ferrite on pit morphology, the critical chloride density below which pits do not propagate, and the critical relative humidity above which pits cannot develop. This data analysis also providing an information on underpinning data of developing the methodologies on pitting propagation rates to inform the operators of nuclear waste stores at IFSFIs of safe conditions of the canisters at present and in future time. The methodology developed in these three papers are flexible and the parameters
can be adjusted to initial experimental time steps sets of the data depends on the experiments conditions (laboratory or field), for realistic predicting the maximum pits growth rate for longer time, including confidence interval round this projection.

• Chapter 9: North Carolina State University as a collaborator is performed experiments to determining the crack growth rate and the stress intensity factor under marine environment (KISCC) for a given load and crack size. Another objective is to evaluate JISCC in marine environment following unloading compliance technique using three-point bend specimens. Crack growth experiments were performed with sensitized SS304H under substitute ocean water at 22, 37 and 60 °C to determine the effect of temperature on crack growth rate. The experiments were conducted on wedge opening loading (WOL) specimens under NaCl and HCl solution to assess the effect of pH on crack growth rate. The effect of chloride on crack growth rate was investigated by comparing the average crack growth rate from the experiments under substitute ocean water and MgCl₂ brine. The experimental crack growth rate for stainless-steel 304H are in the range of 3.0 – 50 mm per year, and for 304L are in range of 1-7 mm per year. Depending on the temperature and pH value.

• Chapter 10: This chapter is summarized the in-situ microscale scale experiments utilizes monochromatic, high-energy x-rays (40<E<120 keV), APS. The microscale experiments design at NCSU with collaboration of Advanced Photonic Source (APS) staff at ANL. The goal is to create 3-D imaging of cracks propagation rates (reconstructed from 2-D), and to extract important information on the fundamental aspects of the SCC crack tip and crack propagation rate. The microscale experiments indicated that crack growth rate for stainless-steel 304H are in the range of 23 - 92 mm per year, which are in the range as of macroscale experiments described in chapter 9. The experiments also show the propagation of phase transformation (γ-Fe, α’-Fe, and ε-Fe) at each location in the vicinities of the crack and tracking the corrosion products formation. Furthermore, due to APS capability of precise measurements of three-dimensional crack morphology. A comparison was made between different crack sizes\dimensions and the detection techniques as described in chapter 7. To determine the precision of various detection and monitoring system (NDT) on the canister surface. More details are given in the report titled as “Synchrotron X-ray Tomography Study of 304 Stainless Steel Cracks”

In summary, this project is generated about 12 publications in various journals, and about 20 publications in a conferences and meetings. Some of the papers presented in this report is still under review. Therefore, this report can be considered as a draft. The report will be updated afterward when the review will be completed, and with additional papers that are not cited in this report.

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Chapter 1
Integrated Research Program Overview on the “Innovative Approaches to Marine Atmospheric Stress Corrosion Cracking Inspection, Evaluation and Modeling in Used-fuel Dry Storage Canisters”

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ABSTRACT

Chloride induced stress corrosion cracking (CISCC) is a concern to the integrity of used fuel dry storage canisters at especially at coastal sites. CISCC has complex interactions associated with environment, stress and materials. The canister surface environment evolves both chemically and thermally through time. The canister experiences applied and residual stresses at macro, meso and micro levels resulting from structural loads, manufacturing, welding, phase changes, and unstable microstructure. Experiments and simulations will be performed using a combination of scientifically derived expressions and stochastic methods to predict future outcomes and their uncertainties: of particular focus will be estimation of inspection intervals necessary to prevent development of an undetected through-going crack. Several innovative techniques will be used including synchrotron x-ray imaging, nonlinear ultrasound waveform analysis, chloride gamma fluorescence, modified implant testing, Gleeble thermomechanical simulation, multi-scale finite element modeling, modified four-point bending tests, and compact tension fracture mechanics tests.

1. INTRODUCTION

1.1 Project Organization and Roadmap

This paper summarized the first-year research accomplished sponsored by DOE Integrated Research Program (IRP), part of consolidated innovative nuclear research program, DE-NE0008442, entitled “Innovative Approach to SCC Inspection and Evaluation of Canister in Dry Storage”. The research team consists of researchers from Colorado School of Mines (CSM); North Carolina State University (NCSU), University of South Carolina (USC); WECTEC Global Project
Services, Westinghouse, an industry partner with vast experience in ISFSI design; Sandia National Laboratory (SNL), Argonne National Laboratory, and Los Alamos National Laboratory (LANL). CSM is leading this project. The overall integrated work management will come predominantly from CSM. The overall relationship between expertise and research disciplines incorporated into the work scope is depicted in the below chart, Figure 1. The members of this team have vast experience in supporting the NRC and DOE concerning dry storage system performance and licensing process. Other capabilities directly related to the project will be developed as well during the project period, and some of them are outlined in this paper.

![Expertise Chart]

Figure 1. Project Team Expertise and Disciplines.

The approach that is adopted in this project consists of five main tasks that break down to several subtasks as described in more detail in following sections in this paper.

1) Data collection and reviewing of existing technical information, and building the database to support the project.
2) Develop unique accelerated lab experiments for Chloride Induced Stress Corrosion cracking (CISCC) evaluation of canister.
3) Develop innovative nondestructive inspection (NDE) tools for CISCC detection.
4) Field experiments and modeling calibration.
5) Predication of CISCC with quantified uncertainty, and an improved probabilistic\ stochastic model.

The project began by establishing a database that will serve as an input to improve the knowledge of the team members. Refining the inspection design of dry storage casks, better understanding of CISCC process and mechanism, and to design laboratory and field tests that closely mimic real
environments that leads to improve our capability to predict canister CISCC, beyond the origin licensing period. In the parallel other tasks is beginning, which ultimately includes characterization of canister materials and environments, sample preparation and testing, mockup and sample modeling, development of an inspection tool (or tools) for monitoring of corrosion from pit initiation up to propagation rate of crack. The gathering and reviewing of the related literatures is vital step for improving the analytical and stochastic modeling of CISCC with quantified uncertainties.

The Figure 2 flowchart below displays the CISCC integrated research topics along the developmental path from laboratory experiments up to data that gathered from the field. Including the employment of inspection tools to assess a canister’s structural integrity. Delineating how the project research study will be developed and how inspection tools will be used to assess the structural integrity of spent fuel storage canisters and adjust the initial prediction models. One of the practical outcome of this project is to allow of independent spent fuel storage installation facilities (ISFSIFs) to manage better the material degradation effect, until repairs can be undertaken at a more economical time or otherwise suitable time for the facility.

This figure captures both the spatial as well as the time-based variability of the corrosion degradation process at canister surfaces in order to be able to quantify the benefit of inspection coverage as well as inspection frequency (time interval). Inspections of the canister represent a highly efficient means of corrosion control and risk reduction of nuclear spent fuel storage at various sites locations. Quantitative corrosion models may form the basis for determining the optimal inspection efforts and economical time (i.e., what to inspect, when to inspect, and how to inspect). Such inspection planning procedures are based on the application of Bayes’ rule to update the uncertain corrosion model using inspection data from the field, due to changes in the chemical, environment and physical characteristics of the material and stress with pit/crack depth and time. This variability is not explicitly modeled prior to inspection (in the laboratory), increasing the scatter in observations, and should be accounted for by the statistical uncertainty model of the corrosion process. Time-based variability due to the inherent characteristics of the corrosion process will therefore be modeled by means of time-invariant random variables. On the other hand, the influencing environmental, material and stress parameters, which in experiments are generally held constant, often vary significantly with time due to the operational conditions of ISFSIs. Future degradation may be different from past degradation, and as such this time-based variability will be addressed in our proposed models. Information obtained from an onsite inspection will be used to update all random variables, which will then be applied for the prediction of future canister deterioration (CISCC).

Since the corrosion process is non-linear in time, it’s very difficult to replicate the corrosion that occurs under actual field conditions at site in laboratory experiments. A more useful approach for risk based inspections of dry storage casks is to develop predictive models based on corrosion science modeling, materials properties and atmospheric marine environments with good quality field data, that will update the future prediction of canister degradation and the measured action need to be taken as indicated the flowchart.
Figure 2. CISCC Analysis and Inspection Path
1.2 Incentives

The general objective of this project is to investigate the potential degradation of austenitic stainless-steel canisters used in dry storage systems for Spent Nuclear Fuel (SNF). Currently SNF is stored in two types of environmental storage conditions; 1) submerged in water in pools at reactor facilities, and 2) in dry storage at Independent Spent Fuel Storage Installations (ISFSIs), adjacent to reactor facilities. Generally, after a few years of cooling time, SNF is removed from the water pool and transferred to helium-filled stainless steel canisters in passively ventilated dry storage systems. As a result of several recent decisions, such as not pursuing Yucca Mountain as a long-term geologic repository storage facility for SNF and the cancellation of the construction of a reprocessing facility in the 1980s due to proliferation risks, interim dry storage facilities for long-term storage are vital for the immediate future of nuclear energy technology. The integrated research program at DOE-NEUP has identified potential deterioration mechanisms for the steel canisters containing the SNF in dry storage that require detailed research and investigation and will have an impact on the performance of long-term interim storage under the normal and extreme environmental conditions experienced during the duration of this storage. The prediction and monitoring of canister corrosion processes while in storage can provide important data for the assessment of interim storage performance and the safety to the public. One of the primary concerns with respect to the long-term performance of the storage casks is the potential for corrosion initiation due to deliquescence of salts deposited on the canister surface as aerosols; in regions of high residual weld stresses, this may lead to localized stress corrosion cracking (SCC). Dust and aerosols in the air being drawn through ventilation openings in the overpack of passively-ventilated dry canister storage systems may be deposited on the stainless steel canister outer surfaces. Under these conditions, localized corrosion attack can occur. Chloride-induced stress corrosion cracking (CISCC) of welded zones is especially of concern, as this is a well-documented mode of attack for austenitic stainless steels (including 304SS and 316SS) in marine environments, and many independent spent fuel storage installations (ISFSIs) are located in coastal areas. Recent canister inspections have shown that chloride salts are present on the surface of in-service canisters in near-marine settings. However, canister surface inspections of sufficient resolution to detect SCC have never been carried out, because access to the canister surfaces through vents in the overpack is extremely limited, and high radiation fields make removal of the canisters from the overpack undesirable. Here, we describe the available information on the canister surface environment and experimental and observational experience with stress corrosion cracking of stainless steels; and identify research needs to accurately predict the occurrence of canister CISCC and to develop a model for evaluating the potential for SNF interim storage canister failure by through-wall CISCC. Then, we propose an experimental program to gather that information. In addition, we propose to develop the necessary technology to evaluate canister surfaces for CISCC within the limited-access dry storage systems.

Figure 3 shows the three necessary conditions for SCC to occur: the metal must be susceptible to SCC, an aggressive environment must exist, and sufficient tensile stress must be present to support SCC. It is expected that these three conditions will be met, at least at some ISFSI sites in near-marine environments, during the period of interim storage, especially if the development of a repository for final disposal is delayed. Although SCC of interim storage canisters has never been observed, that may be largely because detailed canister surface inspections for SCC have never been performed. The welded interim storage canisters are made of austenitic stainless steels which
are susceptible to SCC, and susceptibility is higher in the heat affected zones (HAZ) of welds. Failure of exposed stainless-steel components by CISCC is well-known at near-marine facilities\(^1\). Recent studies at three sites\(^2^3\) indicated that chloride salts are present on the canister surfaces, and if the temperature drops sufficiently for salt deliquescence, a corrosive aqueous environment could potentially occur. Finally, residual tensile stresses will be present in the canisters due to manufacturing processes (rolling and especially welding). While residual stresses in SNF interim storage canisters have never been measured, stress modeling conducted by the NRC\(^4\) indicates that through-wall tensile stresses of sufficient magnitude to sustain SCC are likely to exist in weld HAZ.

![Figure 3. Conditions of SCC initiation and growth](image)

This proposed integrated research project is focused on the prediction of canister CISCC and its effect on canister integrity during long-term interim storage.

1.3 Project Framing

The assessment of the CISCC requires the following of canister characteristics as input: canister stainless steel material composition, heat and cold treatment, microstructure analysis and surface condition, residual and loading stress, and various parameters related to the environmental condition, including information on the average discharge fuel burnup loaded into the canister for evaluation of temperature distribution at the canister surface, which an important factor of chloride deliquesces. Table 1 summarized an example of the range of variable for systematic analysis of CISCC at canister surface. The variables are divided to 3 parts the control one that will be assumed constant during the proposed laboratory experiments, the independent that may varied during the experiments and dependent variable that outcome from the experiments.
Table 1. Various Variables for CISCC Analysis

<table>
<thead>
<tr>
<th>Control Variables</th>
<th>Independent Variables</th>
<th>Dependent Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Properties (Data from Mockup, composition sensitization, cold work, HAZ)</td>
<td>Microstructure &amp; alloy content, canister surface conditions</td>
<td>Pit initiation and growth rate. Pit morphology, and transition to crack</td>
</tr>
<tr>
<td>Residual and Applied Stress</td>
<td>Temperature and RH</td>
<td>Electrochemical Process</td>
</tr>
<tr>
<td>Data on weld and weld repair</td>
<td>NaCl + Mg-SO₄, O, H (Concentration, acidity)</td>
<td>Crack initiation and growth rate, crack morphology, and stopped.</td>
</tr>
<tr>
<td>Data on Canister Fabrication Process.</td>
<td>Wet only; wet/drying fluctuation conditions and Air Flow Rate</td>
<td></td>
</tr>
</tbody>
</table>

2. APPROACH and METHODOLOGY

2.1 Database

The established database help to team member to identify and improve the time prediction of pit/crack initiation and propagation rate, by time scaling between the experiments and theory, which will make the prediction of stochastic model more on physics-based quantitative model rather than solely statistical parametric fit models. It will provide information on assessing the uncertainty of the data and address the issue of error propagation through the experimental results. In summary it will lead to more reliable and accurate of canister materials behavior prediction under various environmental condition at different ISFSIs locations for extended periods. The database comprises of collection and analysis of the existing technical information providing an input to the team researchers in identifying the technology that can be used for CISCC predictive capability for various canister design of dry storage casks in different environmental conditions. The information related to different specimens at different environmental condition that used predict the incubation time and crack propagation rate is reviewed and documented in a computerized database. The general structure of database is give below Figure 4, which divided into two main segment, the internal that generated by member team during the project, mainly from laboratory experimental data, and field data that come out from one location (Maine Yankee). The external one that consisted mainly of articles collection from open literature that arranged by topics. The external database includes also industry standards and guidelines of aging treatment in materials, codes, NRC reports and requirements, technical articles, and presentations, papers at conferences related to the dry storage facilities. The database managed by CSM team and updated routinely by the team members. The advantages of using computerized database are:

- Simple entry and ability to update data upon the availability of experiments and field results.
- Ability to sort and organize dry cask degradation data in a meaningful way.
- Quickly locating the needed information
2.2 Modeling Approach

Lifetime prediction of stainless-steel canister can be based on deterministic or stochastic methodology or on both of them. A brief description of each them given below.

- **Deterministic Approach** - The prediction is based on physics and chemical models the results constrained by natural laws, such as mass and charge conservation and Faraday's law. Point Defect Model (PDM) for growth rate and breakdown of passive film, together with damage function analysis. The PDM has also been used to derive probability density functions (pdf) initiation time for pitting, and growth rate.

- **Stochastic Approach** - The CISCC lifetime describes as the probability of occurrence. The ISFSIs site where localized pitting initiated and propagate occurred randomly and therefore very difficult to predict. The scattering data of pitting initiation and growth rate cannot be avoid even under well-controlled laboratory conditions, therefore it is imperative that experimental data (such as pit nucleation potential) are analyzed from statistical point of view. Various types of probability distribution functions (pdf), have been used and proposed in the literature to analyze the CISCC data, such as Gumbel, Cauchy, and Weibull distribution. Stochastic simulation process of using Markov chain with Monte Carlo shows promising way to simulate the CISCC.

- **Combined elements from Deterministic and Stochastic Approaches**, that will includes some physics base foundation.

The main purpose of our efforts is to establish methods to modeling pitting corrosion that could be used to predict the behavior of canister in dry storage cask for extended period. The strategy adopted in this project involved in investigation both mechanistic/deterministic and stochastic approaches and trying to integrate them into pitting/crack models to estimate canister with stainless
steel type 304 performance. Predictions the performance of canister is inevitably include quantifiable parameter, such as uncertainty or sensitivity. Systematic examination of uncertainty representation through input parameters is needed for a probabilistic model to be defensible.

2.3 Experimental Approach

Two main modes of experiments will conducted in this project: the pitting imitation and growth rate at CSM facility and crack propagation rate at NCSU, which divided into two parts, the macroscale at NCSU facility and microscale with 3-D imaging using X-ray synchrotron tomography at ANL, with the experimental fixture designed by NCSU. These two complementary experiments achieve the following specific goals of (1) evaluate CISCC incubation times by pitting initiation and growing rate testing, transition to crack, and propagation rate, using carefully prepared samples, designed to represent typical canister base metal, weld, and HAZ, residual stress and sensitization; (2) develop fundamental mechanistically based understanding of the factors affecting corrosion crack initiations and growth rates as a function of aqueous salt solution environmental conditions and stainless steel types 304 and 316 properties. The SNL providing data to the team members on samples preparation that based on the full scale canister mockup measurements results, simulating NUHOMS 24P canister (produced at Ranor using procedures established for canisters at Calvert Cliffs ISFSI).

2.4 Experimental Set-Up

Pitting incubation time experiment at CSM

Prior of setting up the pitting incubation time experiments at humidity chamber under controlled accelerated marine environment, experimental evaluation of full size NUHOMS 24P canister is required (input data from SNL). This measured data serves as an input information to the computer simulation code SYSWELD\ABAQUS, to design a replicated experimental specimen that will be inserted into three fog\humidity chambers available at CSM. A preliminary analysis of comparison between mockup measurements data and analytical simulation is summarized in this section. First the residual stress distribution in the mockup caused by multi-pass circumferential and longitudinal welds is analyzed, and then the four-point bending specimens with the aim to replicate the residual stress, and stainless steel 304 properties (microstructure, sensitization, and surface conditions) of mockup. The residual stress simulation of the mockup (12 feet long and 5/8-inch-thick) is performed by ABAQUS depicted in figures 5 (a) and (b) along with the mesh structure. The mockup was constructed by three longitudinal welds as represented by Line 1-3 in Figure 5 (b) and two circumferential welds represented by Line 4 and 5. The multi-pass weld bead morphology is given in Figure 5(d) that was made with three passes from the inside first and the four following passes on the outside.
Figure 5 Modeling of mockup welding procedure with finer meshes near weldments (a) and (b), and schematic drawing of the mockup (c) with the rectangular blocks highlighting the locations of microstructural characterization; (d) Multi-pass bead morphology of weldment.

An example of comparison between the measurement and simulation of residual stress profile along the longitudinal weld depth in the HAZ is plotted in Figure 7. The differences in maximum axial and hoop stress between the measurements and simulation is in the range of 15%-30%. The discrepancy is caused by the simplification of the bead shape adopted in the preliminary simulation trial, and pre-existing residual stress in base metal introduced by rolling process.

Figure 6. Residual stresses in longitudinal weld centerline as a function of mockup depth obtained from modeling and experimental measurements, respectively.

Specimen Design
A four-point bend is design according to ASTM D6272-10. The maximum residual stress of four-point bend specimen is designed to be sited to the maximum longitudinal residual stress observed from mockup measurements. The specimen has a dimension of 16.5×15.9×320 mm³. The imaging of four-point bending specimen geometry with loading frame is shown in figure 7, along with simulated stress (figure 8). The frame will be coated to eliminate any electrical potential that may interfere with electrochemical process within pitting or crack growth rate.

Figure 7. Imaging four points bend specimen

Figure 8. Calculated stress distribution in of four-points bending specimen

In summary further improvement and progress will be made in computer simulation analysis to reduce the gap between the measurement data and simulations.

2.5 Accelerated Crack Growth Rate Experiments - Macroscale (NCSU)

The measurement of $K_{\text{isc}}$ crack growth rate will be performed at NCSU for stainless Steel SS304 and SS304L. A CAD drawing of the corrosion chamber is shown in Figure 9(a), and the actual chamber is shown in Figure 9(b). The length, width, and depth of the chamber were 762 mm x 305 mm x 305 mm (30 in. x 12 in. x 12 in.), respectively. The size of the chamber is sufficient to conduct SCC experiment of up to four samples simultaneously. The ASTM standard E399–12 is used wedge opening loading (WOL) specimen. In this project the direct-current potential drop (DCPD) technique for monitoring crack-growth during $K_{\text{isc}}$ measurement is used based on ASTM E647 standard. For fatigue pre-cracking, the procedures outlined in ASTM E1820-15, E399-12, E1681-03 (2013) were followed as closely as possible. The testing of DCPD system is complete, including the instruments calibration.
2.6 Accelerated Crack Growth Rate Experiments - Microscale (ANL and NCSU)

A complementary experiment to macroscale at NCSU, a microscale experiment of crack morphology and growth rate is designed at ANL with collaboration of NCSU, and the fixture of the proposed experiment is shown in Figure 11. The energy x-ray beam of ~80 KeV will be utilized for 3 dimensional crack imaging. A special environmental cell is designed with the capability of changing the temperature, and relative humidity for various atmospheric sea salt loading conditions, an applied load up to 15 kN, will be used as indicated in Figure 10 below. During loading, the crack front will be followed (using radiography/tomography and the full x-ray beam size) while local microstructure will be mapped with micro beam x-ray diffraction. This procedure will be repeated with different values of relative humidity and temperatures. This unique experiment produces an important fundamental data on crack growth rate under marine atmospheric environment, or on the mechanism that may stopped the crack growth rate.
2.7 Inspection Methodology – Summary of First year Results

Nonlinear Resonant Ultrasound Spectroscopy (NRUS) and the Time Reversed Elastic Nonlinearity Diagnostic (TREND) For Crack Detection.

Two nonlinear acoustic techniques is considered in this project for crack detection. The first, Nonlinear Resonant Ultrasound Spectroscopy (NRUS) is a global used to detect the presence stress-corrosion cracking (SCC) in 304 stainless steel. An efficient means of using NRUS is to excite a selected resonant mode of the sample under test at several vibration amplitudes and measure the resulting changes in the resonance frequency peak and the quality factor (related to damping) of the resonance as a function of the nondestructive excitation levels. The degree to which the resonance frequency changes with excitation amplitude indicates the degree of the overall damage in the sample. The second technique is called the Time Reversed Elastic Nonlinearity Diagnostic (TREND), which uses a technique called Time Reversal (TR) to focus wave energy to various inspection points of interest and then quantify the degree of nonlinearity present at that point. The quantification of the nonlinearity can be done through several techniques. See Figure 11 for an experimental result showing the spatially localized focus produced by TR and for an experimental result of using TREND to image SCC in a Type 304 stainless steel sample. NRUS offers a global inspection technique of the sample, whereas TREND offers a pointwise inspection of the sample.
Figure 11. (a) Experimental result of acoustic wave focusing on an aluminum plate superimposed on a photograph of the sample. (b) Photograph of a stainless steel sample with SCC. (c) TREND image of SCC.

An example of recent experiments that conducted at LANL using NRUS on two samples of steel (304) provided by SNL is shown in Figure 12 along the resonance shift as a function of the source amplitude. It is also clear that the sample with SCC exhibits a more pronounced shift of its resonance frequency than the pristine sample. This shift can be quantify by measurement of the slope of the linear portion of the data is the parameter shown in figure 13. For example $\alpha$ angle of the slope, for the pristine sample, $\alpha = -45$, but for the sample with SCC, $\alpha = -185$, which represents an increase by a factor of 4 compared to the pristine sample, which gives some indication on the extension of the damage.
Figure 12: Images of the SCCs under an optical microscope, along with spectra of the particle velocity measured for 24 source amplitudes around the fourth resonance mode of vibration of the sample: (a) pristine sample; (b) sample with SCC.

Chloride Detection – PGAA and NAA

A detailed of chloride detection methodology and simulation analysis is presented in MS&T16 paper under the title of “SCC DETECTION AND LIFE PREDICTION FOR NUCLEAR WASTE MANAGEMENT USING PGAA AND NAA”. The simulation results with Monte Carlo code indicates that it is possible to detect 7.4 MeV and 6.1 MeV gamma-ray energy results from neutron interaction with chloride, at the outer surface of the concrete overpack of 50 cm thickness in dry storage system. Future work on the proper detector selection and the array around the concrete overpack still need to be determined. Residence time of chlorine on the canister surface needs to be analyzed based on the magnitude of the gamma ray peaks, which corresponds to the neutron fluence inside the canister.

3 SUMMARY and CONCLUSIONS – Project First Year

The assessment study that outlined in this overview paper and in more detailed in accompanying papers presented in various conference, is leading to an improvement in understanding of assessing the impact of CISC on dry storage system life expectation. In the first year of the project identification of canister inspection tools are recognized, such as PGAA and NAA for chloride quantification and NRUS/TREND for crack detection and imaging. Innovative experimental fixture are setup that replicate the canister materials used in ISFSIs, which enhance our understanding of the mechanism that leading to pitting initiation, incubation time, transitions to crack, and crack growth rate or halted it at various marine atmospheric environments.

Acknowledgment

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Chapter 2
Specimens Database Developed for the PROJECT

Laboratory and Field Experiments

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Summary Report

DE-NE0008442, IRP-15-9318
Abstract

The main goal of the database:

- Gathering of literature and reviewing up to date information of chloride-initiated SCC under atmospheric marine environment.

- Assess monitoring techniques of temperature, moisture content, and chloride concentration in marine atmosphere and polluted industrial areas.

- NDE techniques for inspection and monitoring canister remaining life due to pit\crack propagation rate.

- Identify environmental and metallurgical factors that have a significant impact on CISCC. This information will be used to develop the appropriate laboratory testing methodologies for CISCC initiation and growth rate. Develop an algorithm for pit\crack initiation and growth rate for lifetime prediction of canister with appropriate confidence interval.

This databased was very useful. We trained our stochastic algorithms development on the experimental data from the open literature.

The database is closed about six months ago as a result of no funding for continuation of the database development, beside the CSM no other collaborators are utilized it.
Summary of the Database Development and Status

The goal of the collection and analysis of the existing technical information is to provide input to the research effort in identifying the technology that can be used for CISCC predictive capability for various canister design of dry storage casks in different environmental conditions. The information related to different specimens at different environmental condition are used to predict the incubation time of pits transition to cracks, and crack propagation rate was reviewed and documented in a computerized database. An example of the proposed tabulated specimen’s experimental database is given Appendix A, and in various submitted reports to DOE, which includes various stainless-steel material used by canister vendors, the residual stress data in the vicinity of the welding, at different environmental condition. The database also included industry standards and guidelines of aging treatment of canister, codes, NRC reports and requirements, technical articles, presentations, and papers presented at conferences related to the dry storage casks facilities. The data management program “Access” used to manage this wide range of information. The main proposed of the database is to communicate the gathered information among the project participants and other authorized users. The advantages of using computerized database are:

- Simple entry and ability to update data upon the availability of experiments.
- Ability to sort and organize the information on dry cask canister degradation, and to extract relevant data in a meaningful way, to improve the technical dialogue between the participants.
- Quickly locating the needed information, for specific task.

Tabulated listings of reports, papers and other information, type of document, the identification (ID number, will include the dry storage type and the used material), document title, date of publication, author/organization, a summary description, types of dry storage analysis, and potential aging degradation/mitigation issues. The existing available database will be also incorporated, for example from an IAEA database on the dry storage casks in Europe. The collected information will be useful to establish correlation between the various specimens and actual SCC initiation/progress on the canister outer surface. This database improves our fundamental understanding between various parameters that has an impact on canister materials degradation (environment, tensile stress and materials properties). The establish database also improves the coordination between different groups of this project (experimental, theoretical and computational simulation) and identifies the gap in theory and experiments.

The proposed database will help us to improve the time and dimension scales factors between the accelerated experiments environment, and small specimens to actual canister within the field. Improve the theory which and makes the scaling factors more on physics-based quantitative model rather on solely rely on statistical parametric fit models. Provides information on assessing the uncertainty of the data and address the issue of error propagation. Finally, it will help to the projects to be more reliable and accurate of canister materials behavior predication for dry storage casks for extended periods.

This advancement of state of knowledge collection will also contribute to other DOE and NRC related projects.

All collaborators are participated in establishing a database for CISCC of steel storage canisters used for further analysis and incorporation into the probabilistic model for CISCC with uncertainty quantification, underdevelopment at CSN and SNL. A wide range of expertise on the environment and on corrosion of dry storage canisters are provided to the project through National Laboratories, Europe and Japan activities.
on this topic. The approaches that were adopted in this project consist of four main tasks that break down into several subtasks as described in more detail during the three years of the project.

- Data collection and review of existing technical information.
- Develop unique accelerated lab experiments for CISCC evaluation of canister.
- Develop innovative inspection (NDE) tool for pit\crack and CISCC detection.
- Field experiments and modeling calibration.
- Predication of CISCC with quantified uncertainty.

The database is also served as an input for closing the gap of our understanding on CISCC process in dry storage casks, and to design laboratory and field tests that closely mimic real environments, and to improve our capability to predict canister CISCC performance.

Appendix A

Database Evaluation Process for CISCC Project

Presented

By
Necessity of Data Evaluation
Data evaluation is based on available experimental and theoretical evidence, some facts that characterizes to all experimental values:

- Each experimental value has an uncertainty consisting of statistical and systematic components.

- Two or more experimental values usually differ from each other and have different statistical and systematic uncertainties.

- What is the “best” average values from many measurements. (An infinite number of measurements, though of course impossible, would lead to the “true” average value only, if there would be no systematic errors).

- What is the accuracy requirements from the new measurements quantity. (i.e. if, for a given a quantity, many different measurements are already available, only “an order of magnitude” more accurate new measurement can improve the accuracy of the average value for this quantity)

Data Evaluation is an interdisciplinary activity
Data evaluation process is an interdisciplinary activity that requires collaboration and knowledge in the following areas:

- **Experimental material scientist/engineer** (with good knowledge in SCC) and measurement techniques;

- **Theoretical material scientist**: material properties models, SCC and computer codes;

- **Techniques of mathematical statistics**;

- **Programming techniques** for creating, processing and testing **large electronic data files**;

- **Applied sciences and technologies**.

New Data Requirements
To what extent do the existing CISCC and materials properties database fulfill the data requirements for our current project and future dry storage systems, including materials for nuclear waste treatment, and nuclear technology for other applications?

Is the current database enough for dry storage system?
Are the current databases large enough for any storage system?

- There are enough (applicable) experiments to make statistical meaningful calculations of bias and its uncertainty.

- The experiments evenly span the entire range of all the important parameters, without gaps (environment, materials and stress).

- There are enough quality of validated experiments, for the weighting of data for statistical method.

- Better understanding of the material properties behavior at different operating environment conditions of the current dry storage system and the future one.

Material Performance for CISCC Validation (Benchmarking)
Material Performance for CISCC Validation (Benchmarking)

- Are the experiments chosen all high-quality benchmarks from reliable sources?
- Are the experiments chosen taken from multiple independent sources to minimize the possibility of systematic errors?
- Have the experimental uncertainties been provided and used in calculating the bias and bias uncertainty?
- Is the number and distribution of experiments sufficient to establish trends in the bias across the range of parameters?
- Is the number of experiments corresponding with the statistical methodology being used?
Any extrapolation (or interpolation) of the data should be done by means of an established mathematical theory methodology that takes into account the functional of both the bias and its uncertainty.
Developing a fit to data requires the analyst to consider the following questions:

- Is all of the data of equal weight or is some data more reliable than other data?
- What independent variables should be used for developing the fit?
- What types of fits will work?
- How does the analyst know if there is a “good” fit?
Interaction Between Modeling and Experiments

Uncertainty/Sensitivity Analysis
Figure of Merit (FOM) = Growth Rate of CISCC.

\[
\text{Uncertainty} = \frac{\delta \text{FOM}}{\delta \text{Solution}} \left( \frac{\delta \text{Solution}}{\delta \text{Parameter}} \right) \left( \frac{d \text{Parameter Distribution}}{d \text{Experiment Uncertainty}} \right)
\]

We will make an effort to identify the errors in linking between different physical models of different spatial and temporal scales, both on the modeling and experimental sides.

Dynamic Database Structure – Dry Storage Casks
Dynamic Database Structure – Dry Storage Casks
Dynamic Database Structure – Dry Storage Casks
Uncertainty/Sensitivity Analysis

The following are some of the questions from the questionnaire on types and potential effects of uncertainty:

❖ Is there no uncertainty (i.e., is the parameter value well known)?
❖ Are there random errors in measurement?
❖ Are there systematic or biased errors in measurement?
❖ Are there only scarce applicable data or measurements?
❖ Are extrapolations in time or space needed in conditioning the data for use in the system model?
❖ Are underlying models, data, and understanding empirical? Is the theoretical support weak?
❖ Is there natural variability at different times?
❖ Is there natural variability from place to place?
❖ Is there imprecise understanding of the parameter or model?
❖ Are there potential correlations and dependencies that are not quantified?
External Database

A literature search of technical papers, reports, and articles discussing CISCC in dry storage cask will be conducted in an attempt to identify the most current and informative documents about understanding and managing CISCC in canister. The complete results of the literature review will be included in an CISCC literature database.
External Database

Include the following:

- Academic, scholarly journal articles (i.e., peer-reviewed)
- Books
- Conference Proceedings
- Dissertations
- Patents
- Standards
- Technical Reports
- Websites and other Internet Resources
Proposed Folders and Subfolders:

- Different theoretical approaches, methodologies (stochastics, deterministic, both)

Pitting Initiation (Defect Theory, Chloride Ion Dissolution, Local Cells, Stress Theory, Vacancy Theory, Breakdown and Repair)

Pitting Growth Rate

Crack Growth Rate

- CISCC - Laboratory Experiments
  By material, 304, 316, others; stress range; and country (USA, Japan, Europe)

- NDE - Inspection Techniques
  (UT, NAA, Chloride Sniffers, etc.)

- Environmental Data at various ISFSIs

- Standards and Guides (measurements, calibrations, uncertainties - NRC, NIST, ASM etc.)

- RISK Based Information Inspection
External Database

The CISCC Microsoft Access® database???

Search Methodology:

Keywords:

Title:

Author:

Country:

Date:

Source:

Abstract:

Comments and Update:

Link to Actual Document:
Example: Effect of chloride concentration on the critical concentration of dissolved oxygen for SCC in high temperature water

Example
Uncertainty/Sensitivity Analysis

- The relationship between the measured, \( Y \), and \( A, B \) and \( C \) is written most generally as \( Y = f(A,B,C) \).

\[
\begin{align*}
    u_c(y) &= \sqrt{\left( \frac{\partial f}{\partial a} u(a) \right)^2 + \left( \frac{\partial f}{\partial b} u(b) \right)^2 + \left( \frac{\partial f}{\partial c} u(c) \right)^2}
\end{align*}
\]

\( u(a) \), \( u(b) \) and \( u(c) \) are the standard uncertainties of best estimates \( a, b \) and \( c \).
Example: Decay Heat at Canister

Cooling times 12 - 30 years

- BWR assemblies
  number of measurements = 45
  - average $C/E = 1.003 \pm 0.025$
- PWR assemblies
  number of measurements = 38
  average $C/E = 1.011 \pm 0.012$

Pitting Process

- Initiation
- Nucleation of a “metastable pit – Fluctuation in current signal (temporary growth, and then stop (“death”), start/stop/start...sequence
- Propagation – maintaining growth rate (steadily increase in current signal)

Lead to simple idea of connecting the frequency of metastable pit, \( \lambda \) with frequency of formation of “stable” pit \( \Lambda \).

\( \mu \) is the probability of “death”, and \( \tau_c \) is critical age if metastable pit continue to grow for a time longer than \( \tau_c \)

\[ \Lambda = \lambda \exp(-\mu \tau_c) \]
Guide to the Expression of Uncertainty in Measurement


- Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement

Guide to the Expression of Uncertainty in Measurement


Guide to the Expression of Uncertainty in Measurement

Dakota: A Multilevel Parallel Object-Oriented Framework for Design Optimization, Parameter Estimation, Uncertainty Quantification, and Sensitivity Analysis

Version 6.0 Theory Manual

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Guide to the Expression of Uncertainty in Measurement

HISTORY AND VALUE OF UNCERTAINTY AND SENSITIVITY ANALYSES AT THE NUCLEAR REGULATORY COMMISSION AND CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

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Chapter 3
Identification of Sensitized Microstructures in Welds in Spent Nuclear Fuel Containers Using the Controlled Environment Modified Implant Testing Technique

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Abstract

It is of general belief that stress corrosion cracking (SCC) of austenitic stainless-steel type spent nuclear fuel canisters is associated with sensitization. Chromium depletion as a result of \( \text{Cr}_2\text{C}_6 \) precipitation along the weld heat affected zone reduces the corrosion resistance in those locations. These regions can generally be found within a few millimeters from and parallel to the fusion line of the welds. They are, however, small. Pits and cracks will unavoidably propagate into microstructures devoid of \( \text{Cr}_2\text{C}_6 \) making the measurements less
meaningful. For a better characterization of stress corrosion cracking including detailed mechanisms of pitting and pit-to-crack transition under the influence of applied and residual stresses, sizeable samples with the sensitized microstructure need to be available for exposure to the environmental factors, to allow pit formation and eventually to observe cracking. For fracture mechanics testing for $K_{\text{SCC}}$ and $J_{\text{SCC}}$ determination, and for in-situ testing and characterization under synchrotron radiation, the samples should be prepared from a material that contains the unique microstructure that corresponds to that of sensitization. The influence of the corrosive environment (temperature, relative humidity, salt load, flow parameters) and loading conditions on pitting, crack initiation and propagation can then be identified with certainty and related to microstructure.

A major task in the current NEUP research program is to replicate the sensitized material. By first determining the thermal experience (temperature and time) that can reproduce the sensitized microstructure, then sizeable quantities of the material can be produced for other team members for testing. This section of the report will describe the testing techniques used to locate and identify the microstructure that is sensitive to stress corrosion cracking and to determine the temperature range and cooling rates that would produce the microstructure.

A controlled environment modified Implant test was conducted to study SCC in Type 304L stainless steel. A specialized environmental chamber was constructed. A set of test procedures was established and standardized for testing. A thermal model was constructed for the Implant test specimens when exposed to the temperature and time cycles. Some results have been collected and discussed.

Initial experiments were conducted to establish the welding procedures as the standard Implant testing methodology cannot be performed for these tests. The operation of the environmental chamber around Implant testing needed to be developed. The Implant specimens also required salt coating and were then stressed. The last step was to detect the cracks located within the susceptible material. The samples were exposed to several levels of salt loading, applied stress, and ranges of relative humidity. Cracking and corrosion were observed using light optical microscopy (LOM) and scanning electron microscopy (SEM). Vibratory thermography was also used to assist in the detection of cracks. The study to date shows that the modified Implant test is a valid method to duplicate SCC conditions and study atmospheric corrosion and cracking. Pitting and cracking were rapidly initiated. It was able to characterize the sensitized microstructure for the 304L stainless steel samples and the corresponding thermal conditions that produced the sensitized material. These conditions will be validated using Gleeble testing in the next stage of the work followed by heat treatment to produce bulk sensitized materials.

1. **Background**

Stress Corrosion cracking is a complex problem and occurs when the environment, the microstructure of the material, and stress levels are “optimal”, i.e. a combination of all three conditions must be simultaneously
present. The absence of any one of the three either limits the initiation, the corrosion, or the propagation of the crack.

Historically, spent nuclear fuel containers have been fabricated using Type 304 stainless steel plates. The plates were formed into open-ended cylinders and their longitudinal seams welded. These cylindrical rings were then stacked to produce a longer cylinder and the seams around the circumference were then “girth” welded. Due to the welding thermal cycles, the material next to the weld would undergo transformations. Figure 1.0 shows a schematic drawing of a spent nuclear fuel container with the longitudinal and girth welds. This work will attempt to correlate the weld thermal exposure with the developed microstructure in the heat affected zone of the welds as well as the sensitization experienced. Together with the stresses developed during welding and subsequent canister handling, the sensitized microstructure consisted of austenite with precipitated \( \text{Cr}_7\text{C}_6 \) particles and small amounts of deformation-induced martensite contributes to stress corrosion in the corrosive environment.

As a result of the high temperature, the base material near the fusion line may recover and/or recrystallize, and if near enough to the weld, may melt. Softening generally occurs in this region. Further away from the weld there is a region where the kinetics for carbide \( \text{Cr}_7\text{C}_6 \) precipitation is favorable. The material within this region is heat treated to between 450 to 850°C and is commonly known as the sensitized region and under the correct conditions can be more prone to corrosion. The upper and lower limits of the temperature range can change according to the chemical composition carbon content, of the stainless steel. Alloys with lower carbon content will see lower temperatures and longer delay times for carbide precipitation. Residual stresses develop in the canister near the weld from the change in volume in the material as the weld and base material cools. A thermal mechanical model was developed to simulate the conditions in the canister during and after welding. Due to the size of the canister, the complex residual stress states, and ever-changing natural environment, determining the exact location and time when SCC will happen is difficult.
Figure 1.0 Schematic drawing of a spent nuclear fuel container with the longitudinal, circumferential girth welds, and general locations of the heat affected zones.

The Implant test was developed to simulate the weld and HAZ microstructures that result from the welding thermal experience. The basics components of the process consist of a specimen with a spiral notch, a plate of base metal material with a hole, a weld system, and a loading frame to place the specimen in tension. Prior to testing, a cylinder of the same or similar (test) material is machined to have a continuous helical notch down its length. This specimen is then threaded into an armature connected to a load cell. The other threaded end of the specimen will be exposed in the hole of the plate which is supported by the structure of the load frame, so the plate is stationary in all directions. A weld is then deposited on top of the plate joining the specimen to the plate. After welding, a pre-selected tensile load (usually to a fraction of the yield strength of the material) is applied to the specimen until either failure occurs or a specified time has elapsed. No external heating is applied after welding.

During welding, the thermal cycle creates the microstructures like those found in the HAZs of the canister welds within the notched region in the cylinder. Also, during welding, hydrogen can be incorporated into the weld metal which outgasses during solidification. Together with stress and microstructure, hydrogen can promote cold (delayed) cracking and Implant testing is an excellent testing method to evaluate the effect of hydrogen on
weld cold cracking. Material systems can be ranked regarding their resistance to hydrogen cracking depending on the load and time to fracture.

Figure 1.1 shows a threaded cylindrical specimen with a weld bead on top. A tensile load is applied at the conclusion of the welding. Direct temperature measurements and thermal models can be used to determine the thermal history experienced by the specimen. By comparing the thermal history (temperatures) and location of failure, the crack-susceptible microstructure can be identified. The characterization of this sensitized microstructure will be discussed in the remainder of this report. With different applied loads, the times to failure can change. With the knowledge of the thermal history, location of failure and the corresponding microstructure, time to failure and loading condition, the location for post weld inspection can also be determined.

![Fig 1.1](image)

Figure 1.1 A threaded cylindrical specimen with a weld bead on top. A tensile load is applied at the conclusion of the welding. The arrow indicates the direction of loading.

In the present work, the Implant testing was substantially modified with the addition of an environmental chamber to introduce the corrosive elements (salt load, relative humidity, and temperature). To simulate the environment of the canister, salts would be deposited in the threaded region of the welded cylinder and the specimen would be placed into the chamber with preset temperature and humidity. The specimen would then be loaded to a pre-determined stress level. Under load, the notch concentrates the stress to the center of the threads. When the specimen is provided with the proper conditions for corrosion, pitting and cracking can be observed in the notched region. A more detailed discussion of the experimental set up will be presented later in this report.
A thermal mechanical model was developed to simulate the welding process for the Implant test. The thermal histories determined from both models: the canister and the Implant test can be compared. Similar thermal cycles found in the models should produce similar microstructures in both weldments (on the canister and the Implant test). By using the thermal cycle determined from the Implant test model at the location in the threads where pitting corrosion and cracking occurred, a corresponding location for crack-susceptible microstructure can be determined on the model developed for the canister. An examination of the microstructures found in both the canister and Implant test specimen verified that the two models matched well. Grain size as well as degree of sensitization can be used to support the microstructural behavior prediction.

By using the temperature-time profiles determined by the models, bulk material with the crack-susceptible microstructures can then be produced for testing by using the Gleeble or other heat treatment techniques. Testing of this material can lead to the determination of pitting initiation times, crack growth rates, and resistance to cracking once cracks are initiated.

Due to the geometry of the Implant specimen, additional information besides the corrosion and cracking in the HAZ can also be gathered. Hot cracking susceptibility in the weld and along the fusion line can be determined. Since the Implant test specimens are machined, grains with different orientations can be easily observed on the surface of the specimens and characterized. Therefore, cracking susceptibility in the material can be related to the different grain orientations and cold work. This information is important when inspecting damage outside the weld region on the canister.

By comparing corrosion and crack growth rates obtained from Implant testing of different materials, e.g. Type 304 to Type 316 stainless steel, their relative resistance to hot cracking and SCC can be determined. This information can be helpful when selecting materials for the fabrication of these canisters or rejecting delivery of the canisters due to damages that arise from fabrication or mishandling.

For atmospheric SCC testing, the basic Implant testing equipment would be modified. However, the basic fundamentals of the test would remain the same, i.e. a welded threaded specimen is pulled in tension. The major differences are, (1) after welding, the threaded region of the specimen is coated in a corrosive media (salt loading), and (2) instead of ambient conditions, the tensile loading of the specimen is conducted under a controlled environment. By loading the end of this vertical cylindrical specimen of Type 304 stainless steel in the corrosive media, the spiral notch will locate the position of the microstructure most susceptible to cracking. Figure 1.2 shows a schematic drawing depicting the modifications and other possible configurations made to the Implant testing setup for studying SCC. While this study is focused on atmosperic corrosion, this modified Implant test can easily accommodate a variety of different environments and be equipped for monitoring by different non destructive testing methods.
Figure 1.2 Schematic drawing depicting the modifications made to the Implant testing setup for studying atmospheric corrosion.
2. Experimental Setup

This section will give a description of the modified Implant testing equipment and Implant testing procedure.

2.1 Modification to Implant Test Fixture

The Implant test frame was modified so that the test could be done under a controlled environment (atmosphere, temperature and load) for determined time cycles. Figure 2.1 are photographs showing (a) the Implant testing machine and (b) load cell before modifications. The frame is simply a lever arm connected to an actuator and load cell that can apply a static load (in the form of weights on the left-hand side of the set-up.) While suitable for conventional Implant testing, there is no means to hold a controlled environment around a specimen. For this reason, a stainless-steel vessel, Figure 2.2 (a), with a viewing window was fabricated to contain the specimen. Viewing inside the chamber, from the top, shows the fixture used for holding the specimen, Figure 2.2(b). The actuator rod is connected to the load cell holds the specimen centered within the fixture, Figure 2.2(c).

Figure 2.1 Photographs showing (a) the Implant testing machine before modifications. (b) load cell

Figure 2.3 are photographs showing the working modified Implant testing machine. Blower fan, heaters, water injection, dry air injection, and controllers were fitted to the chamber. To maintain a stable environment heating elements and insulations were placed throughout the entire system. Probes to measure the environmental conditions were placed as near to the specimen as possible to help eliminate false measurements of internal variations within the system. Figure 2.4 are photographs showing a heating blanket used to stabilize the environment around the specimen and the mounted humidity/temperature probes near the specimen.
Figure 2.2 Stainless steel containment vessel with a viewing window (a). Top view inside the chamber showing the fixture used for holding the specimen (b). Actuator rod connected to load cell holding the specimen centered within the fixture (c).

Figure 2.3 Photographs showing the Implant testing machine with corrosion chamber modifications and controllers. Front, Side and Back views.
2.2 Implant Specimen

The Implant specimen is a Type 304 stainless steel cylinder machined with a spiral notch as shown in Figure 2.5 (a). Figure 2.5 (b) is a schematic drawing showing the orientation of the weld cup and implant specimen with respect to rolling direction of the base plate. The chemical composition of this specimen is shown in Table 2.1. The specimen would be machined from 0.625 inch thick plate with the direction of rolling. The specimen is approximately 3.5 inches long with a ¼-20 thread on one end and ½-13 thread on the other.

Table 2.1 Chemical composition of Type 304 used in this study.

<table>
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<tr>
<th>Material</th>
<th>C%</th>
<th>Co%</th>
<th>Cr%</th>
<th>Cu%</th>
<th>Mn%</th>
<th>Mo%</th>
<th>N%</th>
<th>N%</th>
<th>P%</th>
<th>S%</th>
<th>Si%</th>
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<tr>
<td>304/304L</td>
<td>0.0216</td>
<td>0.1980</td>
<td>18.3105</td>
<td>0.3915</td>
<td>1.8280</td>
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<td>0.0889</td>
<td>8.1125</td>
<td>0.3250</td>
<td>0.0010</td>
<td>0.2510</td>
</tr>
</tbody>
</table>
2.3 Welding

The specimen was fully cleaned before being threaded into a fixture for securing during welding. Figure 2.6 (a) is a photograph showing the base onto which the specimen was securely threaded for the welding process. Figure 2.6 (b) is a photograph of the specimen with an outer shell (a shield) placed around it. This shell has a small stainless-steel line so inert gas can be routed to the specimen during welding. A weld cup, as shown in Figure 2.6 (c), was placed over the threaded portion of the specimen such that its bottom face rested on the weld fixture. A small amount of 308L stainless steel filler material was placed into the well of the cup. The welding was done using the GTAW process. The torch was held stationary while the welding was performed. Figure 2.6 (d) shows the torch and weld fixture before welding. Welding was performed at 250 A and 25 to 35 V for 4.5 seconds. Industrial grade argon was used for both the welding and back purging of the specimen. A 3/32 inch (8.18 mm) diameter LaYzr tungsten electrode was used to weld with 20 cfh (9.44 L/min) flow rate for shielding at the torch. The purge chamber was set at a flow rate of 1 cfh.

To produce a successful weld, several practical details must be observed. The torch must be centered and held perpendicular (90°) to the specimen. If the torch were tilted or not centered, melting would be uneven around the specimen which would affect the alignment of the loading. Sufficient shielding was also needed to protect...
the root of the weld from oxidation. Figure 2.7 shows photographs of the appearance of an acceptable weld and root. Figure 2.8 shows a specimen that has been oxidized or “sugared”. If the purge gas was flowing at too high a rate, the pressure from the gas would cause the melted pool to blow out resulting in a large hole. Figure 2.9 is photograph showing the cross-section of a completed weld. For convention the

Figure 2.6 Photographs showing welding fixture and setup for welding. (a) weld fixture base, (b) weld fixture shield, (c) assembled weld fixture with weld cup installed, (d) weld fixture and torch before welding.

threads shall be numbered beginning at the fusion line and increasing in number moving away from the fusion line. The weld, fusion line, heat affected zone and base metal are labeled in this figure. Where the base metal and the weld metal meet on the surface, this location will be referred to as the toe of the weld. Since the weld is actually a melt-through, it will be referred to as the root of the weld. The fusion line begins internally in the weld cup and exits towards the threads; this is the region where the heat affected zone meets the weld metal.

Figure 2.7 (a) Completed acceptable looking weld viewed from top into the weld cup. (b) View of acceptable threaded test region and weld root.
During the welding process three clamping conditions can arise. The first, both pin and plate (weld cup) are free to expand and contract without restraint during welding or cooling. Second, pin and plate are fixed during welding or cooling. Third, the pin and plate can both move during welding but are fixed during cooling. The third case fits best the intended testing condition. While the specimen is held by the fixture, the pin is free to expand through the hole in the plate upon heating, and the plate is held by gravity to the fixture. Once the melt pool incorporates both the pin and the plate, and solidification begins, the specimen is deemed as fixed together. As the specimen begins to cool the weld metal has sufficient strength to support the stress in the specimen. The testing conditions will be discussed in more detail in the next section.
Figure 2.9 Photograph showing the cross-section of a completed weld. For convention, the threads shall be numbered beginning at the fusion line and increasing in number as the base material is approached. The weld, fusion line, heat affected zone and base metal are labeled. Where the base metal and the weld metal meet on the surface, this will be referred to as the toe of the weld. Since the weld is actually a melt-through, it will be referred to as the root of the weld. The fusion line begins internally and exits through the surface; this is the region where the HAZ meets weld metal.

Due to difficulty of instrumentation and direct temperature measurements on the specimens during welding, specimen temperatures were not taken in the current experiments. Temperature measurements are being considered for future experiments and methods to reliably collected temperature data will be developed. The current set of tests was designed as a feasibility study to screen out practical difficulties and experimental limitations, in preparation for more scrupulous work.

During the initial weld tests no filler material was added to the weld pool. Hot cracking resulted at the fusion line which was visually obvious. Increasing filler metal additions to the weld pool proved to mitigate the hot cracking situation. The final two specimens of this study used a recycled weld cup. After testing, the weld was machined away from the specimen and cup. The hole in the cup was then repaired using 308L stainless steel filler material. The weld cup was then machined back to dimensions for welding. The welds produced after this repair process showed significantly less sensitivity to hot cracking as compared to those with less dilution.

2.4 Thermal Mechanical Model

A commercial finite elements software, SYSWELD, was used to model the weld thermal experience and stresses developed during the welding process. This software is also able to predict the resulting weld microstructure as
a function of the location on the modeled component. Combining the thermal conditions data with the microstructural evolution history in the specimen, bulk specimens can be created with the targeted microstructural for corrosion susceptibility, pitting-to-cracking transition, fracture mechanics testing, and advanced nondestructive evaluation. These specimens can also be further processed to characterize in-situ corrosion and crack propagation mechanism.

Using as input the welding heat input, physical dimension and geometry of the material, physical material properties, and applying the necessary thermal boundary conditions, SYSWELD was used to model the temperature profiles, microstructure, mechanical properties and the residual stresses developed in the cylindrical specimen.

2.4.1 Model description

Figure 2.10 shows the meshed model used in the finite element analysis (FEA). The Implant test specimen is constituted of three parts: Base metal, weld metal and the screw. All the three parts are made of type 304 stainless steel, for which the material properties are chosen from reference [1]. The cross-section view and top view as shown in Figure 2.10 (a) and Figure 2.10 (c) depict that the base metal (described earlier also as weld cup) is modelled as a cylinder with a hole created in the middle. This hole is consisted by a cylinder on the top and an inverted cone at the bottom. The screw is connected with the base metal at the bottom of the cone. Welding is conducted on the top of the screw and the weld metal is represented by the brown-colored region. As shown in Figure 2.10 (d), the top 10 threads in the screw are meshed with very small size elements to clearly describe the most sensitive region under the thermal and mechanical load. Different parts are connected by the co-node method. The thread is meshed with 4-node tetrahedral elements due to the complicated geometry structure, while the rest is meshed with hexahedral solid elements. The total number of elements is 754,374. The FEA studies for the modified Implant test are conducted using the SYSWELD software.
Figure 2.10 Meshed model for the modified Implant test simulation. (a) Cross-section view. (b) Front view. (c) Top view. (d) Enlarged view.

Figure 2.11 describes the simulation procedures used in SYSWELD. Firstly, spot arc welding is conducted on the top of the screw; the spot welding is realized following a small circular trajectory. During the welding process, the bottom surface of the screw is fixed. After welding, the three pieces are air cooled for sufficient time. At this stage, the ambient temperature is kept as 20 °C with the bottom surface of the screw fixed. Meanwhile, movement of the base metal in the –Y direction is restricted. Then, after cooling, the whole piece is unclamped with three nodes, during which no thermal or mechanical load is applied. Lastly, a uniaxial tensile load is applied to the bottom surface of the screw. The tensile load value is adjusted to achieve a stress level on the screw to be a fraction of the yield strength of the material (250 MPa). During the loading process, movement of the base metal along the –Y direction is also restricted. By taking the four simulation procedures, a process similar to that observed in the experiment is reproduced on the computer. Table 2.1 gives the simulation parameters used in SYSWELD. The choice of these parameters is also closely related to the real conditions in experiment.
Table 2.1 Simulation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Welding Current (A)</th>
<th>Welding voltage (V)</th>
<th>Welding velocity (m/s)</th>
<th>Welding time (s)</th>
<th>Cooling time (s)</th>
<th>Tensile load (MPa)</th>
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<tbody>
<tr>
<td>Value</td>
<td>250</td>
<td>32</td>
<td>0.225</td>
<td>4.534</td>
<td>600</td>
<td>170</td>
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</tbody>
</table>

References


2.4.2 Model Results

Figure 2.12 is a temperature contour map generated by SYSWELD showing the specimen in 3D and a cross-section of the specimen at the end of the welding time. Figure 2.13 is a graph showing the temperature profile at the surface of each thread as a function of time. Figure 2.14 is a series of contour maps showing the development in strain and thermal experience. Note that tensile stresses develop between the fusion line and thread 8. Compression is observed after thread 8. By matching the actual fracture location observed in the modified Implant test specimens with the SYSWELD calculated temperature contours, the region where the microstructure was most sensitive to cracking could be identified. Figure 2.15 are stress contour maps of the specimen upon release from the fixture after cooling, with clear indication that the specimen is loaded during testing. Note the regions in threads 5-8 that does not stress to the same levels as the upper portions of the threads. High surface and subsurface tension in the specimen close to the fusion line may promote crack opening in this region if the microstructure is predisposed to cracking. Thus, it is important to match the microstructure with the developed stresses to confirm the effect of sensitization.
Figure 2.12 Temperature contour maps generated by SYSWELD.

Figure 2.13 Graph showing temperature profile at the surface of each thread as a function of time.
Figure 2.14 Contour maps showing the development in strain and thermal experience along the screw.
3. Experiment

3.1 Description of Experiment

Several experiments were initially conducted to calibrate the equipment and develop a procedure for conducting the modified Implant test. These early tests helped determine the time scale needed to observe cracking, if given the most severe testing conditions. As the test program progressed, the salt load and stress applied on subsequent specimens were reduced, and variations in the relative humidity were controlled. Table 3.1 shows the experimental matrix used for these experiments. As limitations in the procedure were identified, new procedures were developed and adopted, as shown in Table 3.2.
Table 3.1 Experimental matrix

<table>
<thead>
<tr>
<th>Specimen #</th>
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<th>2</th>
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<th>4</th>
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<tr>
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<td><strong>Salt</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type of Salt</td>
<td>Sea Salt</td>
<td>SS/MgCl₂/SS</td>
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<td>Syringe/Dryer</td>
<td>Syringe/Dryer</td>
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<td>1085/2392</td>
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Table 3.2 Experimental matrix for specimen 3

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<td>Filler Material</td>
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<td><strong>Salt</strong></td>
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<td>50</td>
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<td>Relative Humidity R/H (%)</td>
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<td>Duration of Test (hrs)</td>
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<td><strong>Load</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.031”</td>
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<td>Stress (ksi/MPa)</td>
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<td>77.1/531</td>
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3.2 Atmospheric Environment

During the initial test the chamber was able to sustain stable temperature while the relative humidity oscillated, starting high but dropping to lower values. As the tests progressed in number the sources for the fluctuations in humidity were identified and by the final specimen, the relative humidity stabilized attaining the target value of 35%.

3.3 Salt Loading

Initially the salt loading was performed by filling a syringe with a saturated sea water solution. The solution was then deposited into the threads while the specimen was rotated. A heated air dryer was used to evaporate the water. Figure 3.1 (a) is a photograph showing this deposition method. After repeating many cycles of this application method, the result was a salt shell-coated threaded region as shown in Figure 3.1 (b). During this application, the threads would act as an Archimedes screw moving the droplet laterally either towards or away from the weld depending on the direction of rotation. During evaporation the droplet changed in composition precipitating out lower solubility salts as the water content decreased, which led to large variations in local salt composition across the specimen. At times, liquid was observed moving inside the shell. Figure 3.2 (a) and (b) are photographs of specimen 2 after its first round of sea salt coating. Note the uniform appearance and coverage of salt around the threads in Figure 3.2 (a). Figure 3.2 (b) shows the same specimen after testing. The
upper portion of the threaded region (farther away from the weld) appeared to be missing the salt coating. During testing the relative humidity in the chamber reached above 75% and the salt appeared to become a liquid. As the amount of

Figure 3.1 Photographs showing Implant specimen 1 being deposited with a “heavy” coating of salt using a syringe, and the completed specimen

Figure 3.2 An Implant specimen 2 with salt coating. The threads appeared to be missing after the exposure to the test cycle (right-hand side photograph.)
liquid increased a large droplet grew at the base of the stem. With the droplet reaching a critical size, gravity pulled the droplet away from the test region. Since sea salt is comprised mainly of MgCl₂ and NaCl, and since MgCl₂ has a lower solubility in water than NaCl, it is reasonable to believe that the remaining coating is mostly NaCl. Additionally, when pure MgCl₂ was loaded onto a specimen and placed into the chamber, the high humidity caused the salts to become liquid and not remain within the threads.

By decreasing the number of salts applications, the thickness of the salt shell decreased. Visually, the shell appeared to be deposited uniformly but examination with scanning electron microscopy (SEM) quickly revealed local variations in composition. The precipitated NaCl formed large blocky crystals while the remaining salts in the deposit assumed different morphologies. After testing, NaCl crystals in regions with evidence of corrosion appeared to have a “melted” and “flowed” appearance suggesting that the mixture of the salts and corrosion products had a lower solubility in water than the salts alone. This higher fluidity might assist in feeding the corrosion solution to the corrosion front, propagating corrosion and cracking. Corrosion was easy to detect with thick layers of salts. In fact, the salts would become dyed with the corrosion product. Besides the observation of linear features indicating cracks amongst the corrosion products, it was nearly impossible to detect further details without removing the salts.

Figure 3.3 (a) is a SEM micrograph showing an enlarged view of the threaded test region after testing. The salt deposits are the dark features and the lighter regions are the exposed Type 304 stainless steel screw material. The dark corrosive products covered almost the entire specimen leaving only the tips of the threads exposed. Upon visual inspection, variations in salt coating thickness could easily be observed. Figure 3.3 (b) shows the threaded region of specimen 6, which showed lesser corrosion products because of an initially lighter salt coating deposit. Figure 3.4 (a) shows the large blocky NaCl crystals that precipitated during drying.
The final specimen in this study was loaded with salt in a slightly different fashion than the other specimens. One single drop of ASTM standard sea salt solution was deposited into the threads of the specimen. Surface tension between the solution and threads was sufficient to hold the solution such that it did not drip out. The specimen was then introduced into the corrosion chamber with wet threads, stressed while the salts could dry. This procedure resulted in a very thin layer of deposited salts that could not be seen with the naked eye. Visually, the shell appeared to be deposited in a uniform manner but examination with SEM, Figure 3.4 (b), quickly revealed that the specimen had local variations of salt loading.

4. Results

4.1 Corrosion:

Corrosion began in as little as two hours after the tests began. Through the viewing window of the chamber, corrosion could generally be observed beginning at the root of the weld followed by threads 5-8 and the base of the threads. Corrosion was observed on the tips of the threads. When corrosion was observed at the tip of the threads, corrosion would also be observed in the notch down the axis of the specimen.

As mentioned earlier, corrosion was easy to detect with the deposition of a thick layer of salt. Figure 4.1 (a) shows a photograph of a heavily salt coated specimen with discoloration in the region where the threads meet the weld cup (plate). The salts became dyed with the corrosion product. This reddish brown dyed salt helps with quick identification of regions with corrosion. Figure 4.1 (b) shows a magnified image of the dyed salt crust with indication of possible cracking. As the salt crust decreased in thickness, corrosion became less apparent to the
naked eye. At this point, observation of individual evidence of corrosion would not be possible until the salt layer was removed.

Figure 4.1 (a) photograph of a heavily salt coated specimen with discoloration where the threads meet the weld cup. (b) Stereograph image showing corrosion and indication of possible cracking in specimen 1.

Under heavy salt loading, corrosion was found at the base of the threads. This occurrence was mostly caused by the MgCl2 becoming saturated with water and pooling towards the bottom of the threads because of gravity. Heavy corrosion in the shape of the pool remained after the salts were removed. Figure 4.2 is a photograph showing the corrosion at the base of a threaded specimen. Note the linear position of the corrosion indications shaft and of those inside the threads.

Figure 4.2 Photograph showing translucent salt layer with corrosion indications at the base of the threads in the base material.
In specimen 3, the specimen was observed in three steps. This specimen differed from the others by having a “loading and release” step followed by a salt deposition and testing. Threads 6 and 7 showed signs of corrosion in the salt layer after testing. Once the salt was removed the specimen was examined using SEM. Figure 4.3 is a SEM micrograph showing the first 8 threads. The weld is on the left side of the image. Thread 6 had the largest corrosion island and be the dark region in the upper portion of the thread. During examination of this region, the pits appeared to be heavily corroded, with a thick layer of corrosion product filling the well of the pits, Figure 4.4 (a) and (b). While on microscope observation seemed to indicate cracking inside the pits, no verifiable image was able to be produced.

![Figure 4.3](image)

Figure 4.3 SEM micrograph taken of the threaded region of specimen 3. The weld is on the left of the image. Six threads from the weld a dark spot can be seen in the upper portion of the thread.

![Figure 4.1](image)

Figure 4.1 SEM Micrographs showing pitting corrosion in specimen 3, thread 6.
Specimen 6 showed signs of random pitting on the faces of threads 4-8. Threads 5 and 6 had the highest density of this pitting. Figure 4.5 are SEM micrographs showing small salt islands dispersed around larger salt islands (before the salt was removed after testing). After the salts were removed the pits remained. This was the only specimen where this type of pitting behavior was observed. Perhaps the test starting with wet threads vs dry plays an important role in explaining these phenomena.

Figure 4.5 SEM micrographs showing small salt islands dispersed around larger salt islands in threads 5 and 6 of specimen 6.
Figure 4.6 Corrosion appeared to have begun along the grain boundaries. The grains near the fusion zone in the base material appeared to be fully annealed. Strain etching was observed at the grain boundaries.

In regions near the fusion line, i.e. the high temperature HAZ, the material exhibits evidence of annealing. In this region, corrosion was less frequently observed than in other regions. Figure 4.6 is a SEM micrograph showing grains and grain boundaries on the surface of the deformed thread. In the center of this image is a region of a grain showing pitting and the corrosion beginning to travel through the grain boundaries.

Initial stages of corrosion were observed while the corrosion propagated layer by layer (from the surface toward the interior of the plate) and following the corrosion susceptible microstructure into the bulk of the specimen. This observation suggests a different mechanism than that of the formation of a large pit. Figure 4.7 (a) and (b) are micrographs taken from the surface of Specimen 6. The appearance of the corroded surface appeared to be rough and the pits rounded.

Figure 4.8 shows a stereograph image of the threaded region of specimen 2. There appeared to be a crack in the corrosion island but could not be verified due to the extent of the corrosion. This was one of the largest indications measuring close to 0.5 mm. Light optical methods of viewing the corrosion surface proved to be difficult because of the complex specimen geometry and the shallow depth of focus at high magnifications.

Figure 4.7 SEM micrographs showing flaking corrosion in specimen 6.
4.2 Cracking

4.2.1 Hot Cracking

Hot Cracking was observed in the roots of the welds in all specimens. It is of general knowledge that this type of cracking would occur in materials susceptible to hot cracking. As a circular path (albeit small) was followed in performing the spot welds in these experiments, similar stress states as those observed when performing a circular weld patch test for hot cracking susceptibility characterization arise. Hot cracks at the root of the welds near the fusion line appeared to be in sizes both large, Figure 4.9, and small as shown in Figure 4.10. Hot cracking occurs during solidification when solute elements partition from the core of the dendrite to the interdendritic regions. The solidifying material between the dendrites does not have the required strength to overcome the stresses created during cooling. The result is a separation between the dendrites. Figure 4.11 shows a micrograph of a cross-sectioned specimen where hot cracking occurred. The cracks can be seen following the region between the dendrite arms.
Figure 4.9 SEM Micrographs showing large hot cracks in the root of the weld.

Figure 4.10 SEM Micrographs showing small hot cracks in the root of the weld in specimen 5. The melted region is in the upper portion of the image and has the random pointed appearance. The lower section was unmelted thread.
Figure 4.11 Weld root (a) Etched cross-sectional view showing hot cracking, (b) micrograph of polished surface showing cracks, using the backscattered electron detector.

Figure 4.12 is a micrograph taken of the outer surface of the root of the weld with dendrite arms appearing to exit the surface. This micrograph shows that dendrites had grown to the surface of the weld root. The dark material between the dendrites is dried sea salt. During solidification, as the dendrites grow, solutes partition and the alloy composition changes near the interface. The enrichment of solutes at the interdendritic regions may create layers of embrittlement that under stress do not have enough strength to overcome the shrinking forces generated during solidification. Hot cracks were easy to locate after testing because there would always be a corrosion product highlighting this region. The occurrence of hot cracking phenomena in these experiments appeared to reduce in tendency as the ratio of 308L filler material was added to the weld pool. Figure 4.10 shows very small hot cracks at the interface between the melted material and the un-melted base material after the weld cup was reconditioned after previous use with 308L filler material.
Figure 4.12 SEM micrograph showing dendrites growing on the outer face of the root in the specimen. The dark feature is salt which has found its way into between the dendrite arms.

Figure 4.13 Root of specimens 3 at fusion line around partially melted zone. Cracking and corrosion products can be observed in these images. The jagged appearance of the cracks appeared to suggest the possibly of hydrogen involvement.

The micrographs in Figure 4.13 shows cracks that have features of both hot cracking and stress corrosion cracking. These cracks were found at the root of the weld in the partially melted zone along...
the fusion line. Jagged cracks were observed which appeared to not only follow grain boundaries but also cut across the grains, in a transgranular fashion.

4.2.2 Stress Corrosion Cracking

As mentioned earlier in this report, stress corrosion cracks can only appear in the presence of a susceptible microstructure, sufficient stress level, and corrosive environment (salt medium, temperature, relative humidity and time). The simultaneous occurrence of these conditions is required to support stress corrosion cracking. Corrosion is always observed within close proximity of the cracks. Cracks may have originated from corrosion or at least associated with the corrosion products. Figure 4.14 shows two different pits where cracks could be observed to have initiated. In the left image the cracks appeared to have arrested once they extend past the salt deposit. The right image is a micrograph of a pit with regions within the pit that have corroded in a directional fashion. This line of corrosion can be seen extending to the edges of the pit and where it meets the base material and starting a crack. The ends of the cracks appear to be arrested in the material outside the region where the corrosion was occurring.

![Figure 4.14 Micrographs showing the initial stages of corrosion and cracking](image)

Specimen 2 was tested under the harshest conditions (See Table 3.1). It was stressed above its yield strength, loaded with salt such that the test region was fully covered and replenished with fresh salts during the test, and finally loaded and unloaded several times. The result was a specimen with crack down the entire length without much regard to any specific orientation or location. Figure 4.15 is a micrograph showing a stress corrosion crack in the 9th thread. This set of crack appears to have originated from beneath the salt deposit and branched out laterally. It appears that the cracking direction may be related to surface finish and direction of thread machine
marks. The cracking appears be creating a spalling effect in the material. Two small arrows in the upper right of the micrograph are pointing to small cracks connecting between pits.

Figure 4.15 A micrograph showing a stress corrosion crack in the 9th thread of specimen 2. This set of crack appears to have cracks originate from beneath the salt deposit and branch out laterally.

The micrographs in Figure 4.16 show cracking in thread 15 of the same specimen (number 2). The cracks originated near a pit and branched out following the threads circumferentially. The cracks appear to circumferentially propagate though the threads. Figure 4.17 was taken at a higher magnification of the same region showing the lateral propagation. Take note of the delamination of layers as the crack climbs through the material. Figure 4.17 (b) shows a crack originating from beneath the salt deposit and following one of the machining grooves. Figure 4.18 shows cracks starting at a pit and branching circumferentially through the threads.
Figure 4.16 Micrograph showing stress corrosion crack in thread 15 of specimen 2.

Figure 4.17 Electron micrograph showing delaminated layers, cracking and corrosion through susceptible planes. Specimen 2 thread 15.
Figure 4.18 Small cracks propagating from small pits. The corrosion product is observed surrounding the pits. Note the jagged crack morphology. Threads 13,14.

Specimen 5 was tested at 30 ksi (206 MPa) (with reference to 35ksi (241 MPa) YS) and the chamber was relatively stabilized in holding a constant RH. There was a visually continuous layer of salt coating the threads but not filling the grooves. Corrosion products appeared to tint the salt in a band around threads 6 and 7. The two sets of cracks found in thread 6 of this specimen and are shown in Figure 4.19 (a) and (b) The cracks can be seen starting in small pits.

Figure 4.19 Small cracks initiated in thread 6 of specimen 5. These were the only cracks observed down the axis of this specimen.
4.2.3 Linear SCC Indications

Stress corrosion cracking was observed at stress levels of 20 ksi (137 MPa), well below the yield strength. Figure 4.20 shows a set of stitched images taken from the threaded region of Specimen 2. Local corrosion was observed in a line axially down the specimen. Arrows in the figure identify evidence of corrosion and salt deposition. These are the semi-elliptical features in the grooves of the threads, likely a result of the shearing and mechanical working caused by the machining process. As the specimen was extracted from the center of a plate, there may be preferred grain orientations and texture with respect to the direction of rolling. During the machining process the tool cuts through the plate and deforms the grains in a radial direction. The result of this cutting and cold working exposes local sections of the specimen with high energy planes, cold worked material, and residual stress. The semi-elliptical patches are likely the locations (microstructural features) that contain high residual stress as a result of machining or forming at loads well below its yield strength. The rectangular box delineated region shows threads 1 through 6 which do not contain the scalloped shaped corrosion regions as observed further away from the weld. The high temperature in this region caused by the welding likely allowed for the cold work and residual stresses that caused the scalloping to be recovered. Figure 4.21 shows Specimen 6 with the weld on the left side and the base material on the right. Indication of corrosion and cracking appeared down the axis of the specimen in the region delineated by two dashed lines. The long, almost parallel, markings traverse continuously through welded and unmelted material.

Figure 4.20 Three stitched SEM micrographs showing the threaded region of specimen 2. The weld is on the left of the figure and the base material is on the right. The scalloped feature indications preferred corrosion appeared down the axis of the specimens and are delineated by arrows. The region within the dashed box do not show the same scalloped features.
Figure 4.21 Specimen 6. The weld is on the left of the figure and the base material is on the right. Indication of corrosion and cracking appeared orientated down the axis of the specimen in two lines. Locations of corrosion indications in the weld metal continued into the un melted material. These regions are delineated by two dashed lines.

4.3 Crack Detection

Specimens 2, 3, and 4 were sent to Los Alamos National Laboratory to test crack detection using a new nondestructive ultrasonic testing method. High amplitude ultrasonic waves were sent into the specimen causing the cracks to vibrate. The vibrating cracks produce heat and a high resolution infrared camera detects this change in heat. This method is called vibratory thermography. Figure 4.22 shows the Implant specimens attached to the ultrasonic transducer.
Figure 4.22 Figure shows the Implants specimen attached to the ultrasonic transducer used during vibratory thermography testing.

Figure 4.23 Figure shows four images taken using the thermal camera during vibratory thermography testing. The images were all taken from the same specimen and rotated 90 degrees each time. The specimen was rotated clock wise. The arrows indicate the strongest indications found in the threaded region. The images in this figure are in sequential order starting in the upper left quadrant and progressing in a counterclockwise direction. The photographs on the right are of the specimen before the salt was removed and are in the same sequential order.
Images from the four quadrants (defined by rotating the cylindrical sample every 90°), Figure 4.23, show large bright indications at the base of the threads and several smaller indications between the 5th and 8th thread from the weld root position. The brightest of these indications can be seen in quadrants 1, 3, and 4 marked by arrows as shown in the photographs of Figure 4.23. For reference, the threads that contained these small bright indications are shown using arrows in the photographs to their right. No cracking was detected in specimen 3. Specimen 2 did not have a geometry that could be tested.

4.4 Specimen Summary

Implant Test 1

Test Conditions: 51.2 ksi (353 MPa), 24 hrs, Heavy continuous sea salt coating.

Salt was deposited as a liquid through a syringe. The salt solution was then dried using a hair dryer until a thick crust formed. At times, concentrated liquid would form a droplet and drip off the specimen. Unsure of the composition or volume of the droplet would make any salt loading on the specimen unreliable. Corrosion was observed after only 24 hours, generally in and on the edges of the 10th to 12th threads. The sample was cross-sectioned and etched with Aqua Regia (HCl:HNO₃ of 3:1). Hot cracking was the only type of cracking noticed. A dendritic microstructure was observed in the weld zone. No large cracks appeared in the threads. Ferrite stringer ran parallel with the axis of the specimen. Lack of knowledge of what and where to inspect may have resulted in cracks that were missed. It is possible that fine cracks were lost during the etching process since the time was insufficient for growing large cracks. During this test the relative humidity started at 35% and dropped to 20% by the end. The lack of moisture likely slowed the corrosion rate.

Implant Test 2

Test Conditions: 77.1 ksi (531 MPa), 120 hrs, Repeated alternating continuous heavy sea salt and pure MgCl₂ coating.

Cracking and corrosion were observed throughout this specimen. Cracks were found at the weld toes, the HAZ, the base material, and oriented along the axis of the specimen. The severity of cracking throughout the specimen appeared to be proportional to the salt loading, stress state, and duration of the test. The applied stress was well above the yield strength; under the extremely high salt loading conditions, the specimen appeared to have cracks in almost every thread. A large crack was visible under light optical stereoscope at thread 6. SEM was used to detect the smaller cracks throughout the remainder of the specimen.
Implant test 3

Test Conditions: 77.1 ksi (531 MPa), 65 hrs, Heavy continuous sea salt coating.

This study was conducted to determine if cracking was a result of loading the specimen or a combination of loading and salt deposition. This experiment was conducted in three steps and after each step the specimen was observed under the SEM. The specimen was first placed into the load frame and stressed at 77 ksi (530 MPa) for 2 hours. The sample was then removed and examined using SEM. After examination, the sample was coated with salt and returned to the humidity chamber. No cracks were observed after the first two steps. No cracking or corrosion was observed until after a heavy salt coating as in test 1 and test 2 was applied. Heavy corrosion was observed in threads 5 through 8. Cracking was difficult to see due to the heavy corrosion in the pits. This specimen was sent to LANL for NDT but was not able to be tested because of geometric restraints.

Implant Test 4

Test Conditions: 30 ksi (206 MPa), 100 hrs, Heavy continuous sea salt coating.

This sample was sent to LANL for NDT with the salt coating on the surface. Indications of cracking were observed at the toes of the welds and the HAZ. This specimen was tested slightly below the yield strength. The vibratory thermography images revealed a high density of crack indications between threads 5 and 8 with increased severity in threads 6 and 7. The thermal mechanical model (SYSWELD) estimated the highest stresses developed during heating in threads 5 to 8 and that these threads would have experienced temperatures within the region for sensitization, 600 to 400°C. Except for the hot cracks at the toes of the welds, vibratory thermography showed the highest density of indications within this region. Cracking indication at the weld toe could be from a combination of hot cracking and insufficient fusion into the specimen.

Implant Test 5

Test Conditions: 30 ksi (206 MPa), 100 hrs, Heavy continuous sea salt coating.

This specimen was a replica of specimen 4 with regards to the test parameters. Two types of cracks were found in this specimen. As observed earlier, the weld toes showed hot cracks. Cracking was observed in thread 6.

Implant Test 6

Test Conditions: 19.3ksi (133MPa), 100 hrs, Very light intermittent sea salt coating.

This specimen had the lightest salt deposit and most stable environmental conditions. Cracking and corrosion were observed. Corrosion indications were observed in a line down the axis of the specimen. While indications typical to these locations were not entirely unique to the low stresses and light salt loads, these were, however,
the only indications observed in the specimen under the mild conditions and down the entire length of the specimen.
5. Discussion:

Construction and testing the environmental chamber occupied most of the time for this task. Building each piece of the equipment was challenging. No such equipment is available off the shelf. Incorporating the salt loading and standardizing its technique for a cylindrical specimen with machined threads was tedious and sensitive. Uniform coating at a pre-specified salt concentration without large drops dripping off the sample was difficult. Controlling the relative humidity in the chamber with minimum fluctuation was another obstacle. All the challenges have been overcome with a working chamber that is able to maintain temperature and relative humidity to a predetermined programming cycle.

Six modified Implant tests were conducted in this series of experiments to perform the welding; control the chamber; observe the effects of salt loading and stress; and detect crack susceptible material. The first test began with high salt loading, high stress, and swings in relative humidity. By the final specimen the specimen was deposited with light salt loads, stresses below the yield strength and stable relative humidity.

Under high salt loading and high humidity some of the salt would appear to deliquesce. If the amount of liquid salt was large enough, it would form a pool in the threads eventually growing to overcome surface tension to run out of the threads. When the droplets were not large enough, the liquid salt would pool at the bottom of the threads (in the grooves). Thus it was typical to observe corrosion and cracking. Since MgCl$_2$ deliquesces at around 30% RH it would be acceptable to assume that the liquid observed in the threads was MgCl$_2$-rich and that the concentration of this salt plays an important role in the corrosion.

Every specimen showed signs of hot cracking at the toes of the weld. This behavior is expected due to the susceptibility of Type 304 stainless steel to hot cracking and the complex stress state that arises from a circular weld. The extent of hot cracking appeared to decrease as the amount of 308L stainless steel filler material was increased.

Above the yield strength and under extremely high salt loading conditions the specimen appeared to experiencing cracking throughout the specimen. As the conditions decreased in severity the cracking appeared to become more localized. Slightly below the yield strength of the specimen there appeared to be a high density of cracks between threads 5 and 8 with greater concentration in threads 6 and 7. The thermal mechanical model (SYSWELD) showed threads 5 to 8 to have the highest stresses developed during heating. The model also predicted that these threads experienced temperatures within the region for sensitization. Figure 5.1 shows stress and temperature contour maps with photographs of etched samples. The arrows within the sample are pointing to a hazy band that extends across the specimen. This band fits well with the locations of stress and the temperatures calculated by SYSWELD for the material to become sensitized. And finally, with the exception of
the hot cracks at the toes of the welds, vibratory thermography showed the highest density of cracking indications within this same region.

![Figure 5.1](Image)

**Figure 5.1** The thermal mechanical model (SYSWELD) results showing the highest stresses developed during heating in threads 5 to 8 and the temperatures within the region for sensitization.

Below the yield strength and with light salt loads the cracking indications appeared to be linear and local to the axis of the threaded section. While indications typical to these locations were not entirely unique to the low stresses and light salt loads, these were however the only indications observed in the specimen under these mild conditions. The source of these indications were likely a result of the machining process. Since the specimens were extracted from the center of a plate, these indications were likely the result of grain orientations and texture with respect to the direction of rolling. During the machining process the tool cuts through grains orientated normal to the rolling direction and deforms the grains orientated which are orientated parallel to the rolling direction. The grains orientated between these directions will have a mixture of both deformation and cutting. Figure 5.2 shows a graphical representation or the extracted implant specimen relative to the orientation of the rolling direction of the base material. The result of this cutting and cold working exposes local sections of the specimen with high energy planes, cold worked material, and residual stress. The cold worked material has a high probability of containing strain-induced martensite with respect to the rest of the specimen. Since corrosion and cracking did not seem to appear to be more prevalent in the sensitized region, it is possible that SCC is more susceptible in this type of microstructure with these specific grain orientations to the exposed environment. These locations appear after the tool finishes smearing and cutting begins again.
Figure 5.2 shows a graphical representation or the extracted implant specimen relative to the orientation of the rolling.

ABIQUIS was used to model the thermal experience and stresses that developed during welding in an actual canister. The model was developed based off of the conditions that used to fabricate a mockup canister. It was found that there is a 16 mm wide region next to the weld beginning 22 mm from the weld centerline which experienced sensitizing temperatures within the range of 850-450°C. This band correlates well with the location of cracking in the sensitized region of the implant specimen where also the temperature range was found to be within the 850-450°C range. Figure 5.3 shows the comparison between the thermal experience of the implant specimen and the welded canister. By narrowing down the crack susceptible microstructure in the implant specimens to a location between threads 5-8, the location of the crack susceptible microstructure in the canister could be assumed to be within the 16mm band as before mentioned. Inspections should focus on the material within and around the periphery this band. Locations which have visible damage within this region, e.g. dents, gouges, deep scratches, or grooves, should be examined even more thoroughly since the presence of strain induced martensite, contamination, stress risers, and local residual stress is much more likely.
Figure 5.3 showing the comparison between the thermal experience of the implant specimen and the welded canister. The graph in the bottom left corner was generated using ABIQUIS. The color contour map of the implant specimen in the upper right corner was created using SYSWELD. The figure in the upper left corner shows a graphical representation of the intersection at a longitudinal and circumferential weld.

Not all canisters were built the same and to create a computer model for each canister may be at best difficult if the original fabrication documents can even be located. The Feritscope was developed to determine the ferrite percentage in metals based off a magnetic response. It just so happens that the Feritscope can not only detect the ferrite but also the strain induced martensite that is produced during the rolling process. The Feritscope cannot distinguish the difference between the ferrite and the martensite. A section of the mockup canister was tested using the Feritscope and the results were plotted as a color contour map. The data in Figure 5.4 shows that the bulk of the canister had a higher ferrite percentage (yellow–red color) where as next to the weld the percentage of ferrite was much less (blue and grey). Assuming that the surface of the canister started with a uniform distribution of ferrite any changes in measurement would be due to the formation of the strain induced martensite. It has been found in literature that the reversion
Figure 5.4 Feritscope measurements are shown in the contour map superimposed on the canisters surface. Martensite reversal can be observed in the HAZ adjacent to the weld where the ferrite number changes from high to low or the color changes from yellow to blue. Thermal history with the martensite reversion temperatures is shown graphically in the lower left corner. Lines of strain induced martensite from the bump forming process can be observed in regions where there is a local increase in ferrite number or the color changes from yellow to red.

of martensite begins around 400°C. By superimposing the results of the thermal model of the canister and the results of the Feritscope measurements the drop-in ferrite percentage next to the weld correlates well with the thermal experience. By locating where the martensite begins to revert on the canister the thermal experience can be extrapolated to find the location where 400°C was reached during welding. 450°C is where sensitization begins. Starting where the martensite begins to revert, the HAZ between that and the weld metal is where the sensitization is most likely to be found. Without prior knowledge of the canister’s fabrication processing conditions one can use the Feritscope to predict where the sensitization begins, the degree of strain induced martensite caused by the forming process, and the degree of damage caused by dents or gouges.
6. Conclusions:

Cracking and corrosion were observed in all six specimens. Typically, cracks were found in four locations, 1) weld toes, 2) HAZ, 3) base material and 4) along the axis of the specimen. The severity of cracking throughout the specimen appeared to be proportional to the salt loading, stress state, and duration of the test. Threads 5 to 8 showed the greatest number of corrosion and cracking indications. The thermal model (SYSWELD) suggests that both temperature and stress state play a strong role in sensitization in this region. This phenomenon could be analogous to strain aging in other materials where the strain and temperature assist in the formation of precipitates.

Study to date tends to suggest that there are three possible scenarios for cracking in the spent fuel containers; (1) Hot cracks and grain boundary defects at or near fusion line (inherent to the material); (2) Stress corrosion cracks in sensitized material starting slightly below the yield stress; (3) Generalized stress corrosion cracks, at location of high residual stress, exposed high energy planes, salt and moisture.

By vertically loading a salt coated cylindrical specimen of Type 304 stainless steel and placing it into a controlled environment, different types of cracking and their predominant locations were identified. In-depth analyses of the microstructure (major phases and precipitates), volume fraction, and chemical constitution can now be conducted. Corrosion products and defects (type, size, shape, and location) can also be characterized. Having a stable environment and controlled salt deposition is crucial in the development of base rate expressions for predicting pitting and cracking behavior of the canister material.

This version of the modified Implant test is suitable for predicting SCC and hot cracking behavior. It is possible to identify the temperature-time cycle for the production of bulk materials that contain sensitized 304L stainless steel materials for fracture mechanics testing, in-situ crack tip characterization, nondestructive testing of defects, and stress corrosion testing.

7. Future and Continuing Work

An ultrasonic humidifying chamber has been constructed as an alternative method for salt deposition. This method is advantageous over the syringe method since the salt layer deposited is much more uniform. The typical size of the salt deposited using the syringe was on the order of hundreds of micrometers across and the average space between the deposits similar. Using the ultrasonic method the average size particle was found to be between 1-10 micrometers across. Figure 7.1 shows the ultrasonic humidifier, chamber, and a positioner for rotating the specimen during the salt application. The results of different salt application times on flat plates are show in Figure 7.2. The top set of images were measured to be loaded at 4 g/m2, the middle images at 2 g/m2
and the bottom set of images around 0.1 g/m². Correlating these images to the salt deposited on the implant specimen will allow us to measure the salt load. Having an even and consistent coating of salt will help with more accurately determining the pitting initiation times and crack growth rates in future experiments.

Figure 7.1 Photograph showing the ultrasonic humidifier, chamber, and a positioner for rotating the specimen during the salt application.
Figure 7.2 SEM micrographs showing salt applied to flat sheets with the loading (a) 4 g/m², (b) 2 g/m² and (c) 0.1 g/m². The images in the left column were taken at a magnification of 500X and the images in the right column were taken at 1000X.

Microstructural evaluation of the size and distribution of the carbides will be conducted on the implant specimen, mockup canister, and artificially generated specimens. This data will then be fed back into the ABIQUIS and SYSWELD models to more accurately predict the formation of carbides in the HAZ.
Chapter 4
Specimens Database Developed for the PROJECT

Laboratory and Field Experiments

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Abstract

A total of 19 large 4-point bend specimens, all were loaded to the same level (250MPa Max.). 8 out of the 19 were placed at Maine Yankee. Two large 4pb samples were sent to Sandia, including one 304 L polished, and one 304 H polished for electrochemical potential mapping. 9 samples were placed in the CSM humidity chamber at 50°C, 35% RH in early August 2017. One 304 L polished samples was taken out on Oct. 30, 2017 and sent to Sandia for pit morphology characterization. In addition, 24 small 4-point bend specimens with different surface and load conditions but all the same material, 304 L, were placed at Maine Yankee.

More details on specimen’s production stress analysis is given in the final report submitted to DOE on the “Weld Residual Stress Analysis in the Canister Mockup” in April 2018.

Appendix A – Describes the procedure of specimens prior the actual installation and actual installation work at Maine Yankee.

Summary of the loaded large 4pb specimens

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Note:

- SC—surface condition
- MS—Maximum stress load
- HCN—Humidity Chamber number
- MY—Maine Yankee
- CSM1,2—CSM chamber number
- I—Inlet
Summary of the loaded small 4pb specimens.

All these samples have been placed at Maine Yankee site on Sep.1, 2017.

Small 4pb samples

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<td>24</td>
<td>304L</td>
<td>Mill</td>
<td>310</td>
<td>MY#O#H#B</td>
</tr>
</tbody>
</table>

Note:

SC—surface condition (36#, 60#, Polished, Mill)
MS—Maximum stress
HCN#—Humidity Chamber number
MY#—Maine Yankee
I—Inlet
O—Outlet
H—Hot
C—Cool
B—Block wind
P—Prevailing wind
Specimens installed at Maine Yankee.

**Large 4pbt samples: 8 specimens at the same load level (250MPa Max.)**

<table>
<thead>
<tr>
<th>Bottom (inlet)</th>
<th>High temp (sheltered)</th>
<th>High temp (not sheltered)</th>
<th>Low temp (sheltered)</th>
<th>Low Temp (not sheltered)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 304L Mill</td>
<td>2. Wc</td>
<td>3. WL</td>
<td>4. 304L SF1</td>
<td></td>
</tr>
<tr>
<td>Top (outlet)</td>
<td>5. 304L, Mill</td>
<td>6. 304L, SF3</td>
<td>7. 304H, SF3</td>
<td>8. 304L, SF1</td>
</tr>
</tbody>
</table>

**Small 4pbt samples: Total 24 specimens, with the same material (304 L)**

<table>
<thead>
<tr>
<th>Bottom (inlet)</th>
<th>High Temperature (sheltered)</th>
<th>High temperature (not)</th>
<th>Low temperature (sheltered)</th>
<th>Low temperature (not)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Mill (310MPa, 240MPa, 150MPa)</td>
<td>2. SF1 (310MPa, 240MPa, 150MPa)</td>
<td>3. SF2 (310MPa, 240MPa, 150MPa)</td>
<td>4. SF3 (310MPa, 240MPa, 150MPa)</td>
<td></td>
</tr>
<tr>
<td>Top (outlet)</td>
<td>5. Mill (310MPa, 240MPa, 150MPa)</td>
<td>6. SF1 (310MPa, 240MPa, 150MPa)</td>
<td>7. SF2 (310MPa, 240MPa, 150MPa)</td>
<td>8. SF3 (310MPa, 240MPa, 150MPa)</td>
</tr>
</tbody>
</table>

Note: SF1, SF2, SF3 refer to three surface finish conditions, i.e. #36, #60, mirror. Wc, WL refer to the circumferential and longitudinal welds cut from the mockup.
New 4pb samples loaded during 2018

Total 40 large 4pb samples currently with the mill surface condition. 304L: Ten cut parallel to the rolling direction (RD), and ten perpendicular to RD. 304H: Ten cut parallel to RD, and ten perpendicular to RD Total 6 small 4pb 304L samples. Two 36# surface grit, two 60# surface grit and two polished surface condition. All have been welded along the center line by Scott Gordon.

<table>
<thead>
<tr>
<th>Tag number</th>
<th>Material</th>
<th>SC</th>
<th>MS (MPa)</th>
<th>Weld Type</th>
<th>HCN#</th>
<th>Salt Load (g/m²)</th>
<th>RD (∥ or ⊥)</th>
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</thead>
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<tr>
<td>2</td>
<td>304H</td>
<td>Mill</td>
<td>250</td>
<td>CSM2</td>
<td></td>
<td>4</td>
<td>⊥</td>
</tr>
<tr>
<td>20</td>
<td>304H</td>
<td>Mill</td>
<td>250</td>
<td>CSM2</td>
<td></td>
<td>2</td>
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<td>3</td>
<td>304L</td>
<td>Polished</td>
<td>250</td>
<td>CSM2</td>
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<td>4</td>
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<td>23</td>
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<td>36#</td>
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<td>CSM2</td>
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<td></td>
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<td>250</td>
<td>CSM2</td>
<td></td>
<td>4</td>
<td>⊥</td>
</tr>
</tbody>
</table>

Samples 20-25 highlighted in orange are the new ones to be loaded.

Small coupons for the pitting initiation testing
Eight coupons of 2” long, 1” wide, and 5/8” thick are machined and polished, to examine pitting initiation sites influenced by:

- Salt load: 2g/m$^2$ vs 4g/m$^2$
- Microstructure: base metal, and sensitized microstructure by heating the base metal in furnace at 600˚C for 100hrs.

**Summary of small coupon conditions**
<table>
<thead>
<tr>
<th>Tag number</th>
<th>Material</th>
<th>SC</th>
<th>MS (MPa)</th>
<th>Sensitized condition (Y/N)</th>
<th>HC#</th>
<th>Salt load (g/m^2)</th>
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<tr>
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<td>600 C sensitized</td>
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<td>Weld cross section covering from BM to weld zone</td>
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<td>SC-10</td>
<td>Weld cross section covering from BM to weld zone</td>
<td></td>
<td></td>
<td></td>
<td>CSM1</td>
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Appendix A
Preparation of Specimens Installation at Maine Yankee

Maine Yankee Samples Placement
Proposed Sample Geometry, Number and Locations Per Canister

- 4 point bend specimens
  - Large
    - Inlet
    - Outlet
  - Small
    - Inlet
    - Outlet
    - Middle
- Atmospheric Dust Sampling and Dust Loading
  - Collection Plate
    - Inlet
    - Outlet

Proposed Sample Geometry, Number and Locations Per Canister

- Large 4 point bend specimens
  - Inlet
    - 1 ea
  - Outlet
    - 1 ea

Specimens will be placed in the flat position as shown above.
Proposed Sample Geometry, Number and Locations Per Canister

- Small 4 point bend specimens with 3 different stress levels
  - Inlet
    - 4 ea
  - Outlet
    - 3 ea

Specimens will be placed in the vertical position with the tension portion of the specimen facing up.

Proposed Sample Geometry, Number and Locations Per Canister

- Small 4 point bend specimens
  - Middle
    - 3 ea
    - Different loads

Offset pins to keep samples off canister walls

Stainless steel cable to connection outside canister as per recommendation

Typical 316 Stainless steel cable connectors
Proposed Sample Geometry, Number and Locations Per Canister

- Atmospheric Dust Sampling
  - Inlet
    - 1 pc in each inlet
  - Outlet
    - 1 pc in each outlet
Proposed Sample Geometry, Number and Locations Per Canister

• 4 point bend specimens
  – Large (2 ea)
    • Inlet (1 ea)
    • Outlet (1 ea)
  – Small (9 ea)
    • Inlet (3 ea)
    • Outlet (3 ea)
    • Middle (3 ea)

• Atmospheric Dust Sampling and Dust Loading
  – Collection Plates (8 total)
    • Inlet (1 ea per inlet)
    • Outlet (1 ea per outlet)

Duration and Observation Schedule

• Samples will be pulled at year 1 & 2 for examination w/o destroying the samples and replaced after examination. Tests will include
  – Visual Testing
  – NDT
    • Ultrasonic, Eddy Current
  – SEM
  – XRD

• To gather a more complete data set, samples shall be pulled for further examination at later dates and the frequency is TBD
Questions regarding the number of additional samples that should be placed around different locations at the site

How many sample locations per container? How many sample locations at the site?

We would like to place samples in 4 different containers around the site: 2 containers that have been most recently loaded (Hot) and 2 containers that have been in service for the longest amount of time (cold). In both the hot and cold containers we would like two different conditions, one directly exposed to the prevailing winds and the other sheltered from the prevailing winds.
Appendix A

Installation Process at Maine Yankee

The installation process was described by serious of pictures given below, all the administrative process prior to installation including all security and safety precaution guidelines during the installation process is available at Maine Yankee upon the proper request. The pictures speak by themselves.
OWNER: MAINE YANKEE ATOMIC POWER CO.
DESIGNER: NAC INTERNATIONAL INC.
FABRICATOR: P.M.R.I.

DATE OF MANUFACTURE: 10/19/01
MODEL NUMBER: UMS-SO
CASK NO.: MY-VCC-56
DATE OF LOADING: 03/13/02

EMPTY WEIGHT: 221,696 LBS.
100,560 KG.
Chapter 5
Final Report: Weld Residual Stress Analysis in the Canister Mockup

For Project: Innovative Approach to SCC Inspection and Evaluation of Canister in Dry Storage

Prepared for U.S. Department of Energy Nuclear Energy University Program

DE-NE0008442 of Integrated Research Program No. IRP-15-9318

Colorado School of Mines
Golden, CO  80401

Xin Wu, Zhenzhen Yu

April 29, 2018
SUMMARY

Chloride-induced stress corrosion cracking (CISCC) in the weldments of austenitic stainless steel canisters is one of the primary safety concerns during the dry storage of used nuclear fuel at Independent Spent Fuel Storage Installations (ISFSI) in coastal areas. Lifetime extension of the dry storage canisters requires a fundamental understanding of the behavior of the canister material in corrosive environment and stressed conditions and the ability to accurately predict and monitor material degradation so that corrective maintenance actions can be taken. This report summarizes the progress in 2017 on (1) weld-induced residual stress simulation in the mockup, (2) replication of the stresses experienced by mockup materials through four-point bending test for laboratory and field experiments, finite element (FE) analysis of (3) pit morphology effects on stress/strain concentration in the mockup canister and (4) stress/strain distribution around a crack tip in a pre-cracked SCC tensile specimen.

1) FE models were built to simulate the multi-pass welding process with a double-V groove and crossing longitudinal and circumferential welds using ABAQUS software. The calculated residual stresses matched well with the experimental measurements using deep-hole drilling (DHD) and contour methods provided by the collaborators at Sandia National Laboratories (SNL) [1]. Sensitivity analysis was performed to evaluate the influence of model input parameters on the variation of maximum residual stress levels in the weldment and heat-affected zone.

2) A modified four-point bending (FPB) setup was designed to identify the effects of stress on pitting and cracking behavior. Digital image correlation (DIC) method was used to monitor the strain contours during incremental loading on the FPB specimens. A set of modified FPB specimens have been placed in humidity chambers under two different salt loads and a fixed humidity level. For field test, in addition to the modified FPB specimens, conventional FPB specimens simulating three stress levels in base metals were also prepared and placed at the Maine Yankee depository.

3) Influence of pit morphology on localized stress concentration in the weldments was examined by FE modeling. The results will provide important insights for understanding the pit-to-crack transition.

4) FE analysis was performed on the pre-cracked specimens under different tensile loads in a corrosive environment to provide the stress and strain distributions around the crack tip and the prediction of critical J integral value, which is critical for understanding the stress corrosion crack propagation behavior observed by in-situ synchrotron x-ray measurements.
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Figure 1: (a) The FEA model for the mockup with fine meshes near welds, and (b) schematic drawing of the mockup.   

Figure 2. Experimental bead morphology and the corresponding computational weld bead.   

Figure 3: Heat source model used for weld simulation [11].   

Figure 4 Temperature contours of individual weld pass in the longitudinal welds: (a) inner passes, (b) outer passes, and (c) comparison of fusion boundary between simulation and experimental observation.   

Figure 5 Overall residual stress contours for (a) axial stress and (b) hoop stress from FEA.   

Figure 6: Residual stress profiles as a function of depth in (a) weld centerline and (b) HAZ of circumferential weld from FE simulation (dashed lines) and DHD measurements (solid lines). The data of FE simulation is averaged from ten points in the steady state location.   

Figure 7: Cross-sectional hoop stress maps for circumferential weld from (a) contour method and (b) FE model.   

Figure 8: Residual stresses profiles in (a) weld centerline and (b) HAZ of longitudinal weld from FEA (dashed lines) and DHD measurements (solid lines). The data of FEA is averaged from ten points in the steady state location.   

Figure 9: Cross-sectional axial stress contour distributions for longitudinal weld from (a) contour method and (b) FEA.   

Figure 10: Two data collection sites for the longitudinal weld in sensitive study.   

Figure 11: Temperature-dependent Young’s modulus from different material databases.   

Figure 12: Temperature-dependent thermal expansion coefficient from different material databases.   

Figure 13: Temperature-dependent specific heat from different material databases.   

Figure 14: Temperature-dependent thermal conductivity from different material databases.   

Figure 15: Axial stress distributions in longitudinal welds generated by material properties from different references: (a) CMS, (b) JMP, (c) FED and (d) NRC.   

Figure 16: Hoop residual stress as a function of thickness in weld centerline generated by material properties from different references in comparison to the DHD measurement result.   

Figure 17: hoop residual stress as a function of thickness in HAZ using material properties from different references in comparison to the DHD measurement result.   

Figure 18: Axial stress distributions in multi-pass longitudinal welds with (a) one-direction, and (b) back and forth welding processes.   

Figure 19: Axial residual stresses as a function of thickness in the weld centerline using one-direction and back-and-forth welding methods.   

Figure 20: Axial residual stresses as a function of thickness in HAZ using one-direction and back-and-forth welding methods.   

Figure 21: Axial stress contours in longitudinal welds with different time intervals in-between passes.   

Figure 22: Axial residual stress along the depth direction in the weld centerline with different time intervals in-between passes.   

Figure 23: Axial residual stress along the depth direction in the HAZ with different time intervals in-between passes.   

Figure 24: Geometry of the canisters in (a) vertical and (b) horizontal positions and the (c) coupling between point mass and canister.   

Figure 25: Contour stress distributions within the canister in vertical position under gravity: (a) radial stress, (b) hoop stress, and (c) axial stress.   

Figure 26: Contour stress distributions within the canister in horizontal position under gravity: (a) radial stress, (b) hoop stress, and (c) axial stress.
Figure 27: (a) A modified four-point bending setup with the sampling area highlighted by green and red colors. The red color indicates tensile stress region, while the green color indicates compressive stress region. The plate in gray represents the base metal. TD, RD and ND stand for transverse, rolling and normal directions, respectively. (b) Schematic drawing of the mockup with three longitudinal and two circumferential multi-pass welds.

Figure 28: Axial residual stress distribution: (a) on the outer surface as a function of distance away from the weld centerline, and (b) on the cross-section of the mockup multi-pass longitudinal weld.

Figure 29: Optimized geometry of the modified FPB setup by FEA.

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Figure 31: (a) Photograph of the DIC setup for FPB testing, and (b) the speckle pattern on the side surface of FPB setup prepared for DIC analysis.

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**ACRONYMS**

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1. INTRODUCTION

Chloride-induced stress corrosion cracking (CISCC) in the weldments of austenitic stainless steel canisters is one of the primary safety concerns during the dry storage of spent nuclear fuel (SNF) at Independent Spent Fuel Storage Installations (ISFSI) in coastal areas [1,2]. For SCC to occur, three criteria must be met: an aggressive chemical environment, susceptible microstructure, and sufficient tensile stress. Field sampling analysis of surface deposits on in-service SNF storage canisters at three near-marine ISFSI sites in the United States have demonstrated the presence of chloride-rich salts on the canister surfaces [3,4]. As canister surface locations cool sufficiently for the salts to deliquesce, a chloride-rich brine could form locally on the surface providing the required aggressive surface environment. Moreover, the multi-pass welding procedure used for the austenitic stainless steel SNF interim canisters introduces high through-wall tensile residual stresses [3-6], and also introduces microstructural changes (sensitization) in the heat-affected zone (HAZ) that increase metal susceptibility to corrosion. The combination of these factors can lead to potential through-wall failures by CISCC in the weldments of the stainless steel interim storage canisters.

To gain a fundamental understanding of the pitting and cracking behavior in the canisters and accurately predict their long-term performance, the first step is to obtain the residual stress distribution within the canisters, especially in the weldments. In the last decade, there have been several studies on the residual stress in the canister welds. For example, Kosaki et al. [7] reported that the experimentally measured maximum residual stress was close to the yield point on a cylindrical canister of 1.3 m in diameter and ~75mm in thickness. Kusnick et al. [8] simulated the residual stresses for typical canister welds by employing a two-dimensional sequentially coupled thermal-structural finite element (FE) model, and predicted that tensile stresses of sufficient magnitude to initiate SCC are likely to present in the HAZ of both longitudinal and circumferential welds through the wall thickness of the canisters, allowing for crack propagation through the wall thickness over time. There is very limited literature on 3D simulation of the residual stress induced by multi-pass longitudinal and circumferential welds in the dry storage canisters. In this study, a 3D FE model using ABAQUS software was built to simulate the residual stresses in the 304 stainless steel canisters with the presence of both longitudinal and circumferential multi-pass welds. Experimental measurements by deep-hole drilling (DHD) and contour methods provided valuable comparisons with the simulation results. The residual stress model provided critical inputs for the following stress replication experiments and analysis on pit morphology influence. The stresses experienced by the mockup weldments was replicated to laboratory scale specimens through four-point bending test. The influence of pit morphology on localized stress concentration was analyzed as well by FE modeling. The results will provide important insights for understanding the pit-to-crack transition.
2. WELD-INDUCED RESIDUAL STRESSES

2.1 3D Model of Multi-Pass Welding Process

2.1.1 Simulation Geometry

ABAQUS software was used to build the residual stress models for longitudinal and circumferential double-V groove multi-pass welds. Figure 1(a) demonstrates the meshed structure with 52100 brick elements established based on the actual geometry of the mockup and the welding conditions as schematically illustrated in Figure 1(b). The mockup consists of three cylindrical shells that were 12 feet long and 5/8 inch thick as shown in Figure 1(b). The shells were rolled from a plate into a cylinder and then welded at the longitudinal seam. The three cylinders were joined together by two circumferential welds. Details of the welding parameters including pass sequence, voltage, current, travel speed and heat input for each weld pass are listed in Table 1, which were provided by the collaborators at SNL. Take longitudinal welds for example, the three inner passes were made first, followed by the four passes in outer diameters. Since the three longitudinal welds were arranged 180 degrees apart and the two circumferential welds were separated by the middle section, the interference between the same welding types can be negligible. Hence, in this FE model, only the longitudinal and circumferential intersecting joint in half of the mockup section was simulated, as shown in Figure 1(a), and the welding length was sufficient to reach steady state. Note that the heat source traveled through the whole length of the welds to make sure the elements experience the same thermal history as the actual welds did. The repair welds were not considered due to the lack in welding parameter information.

![Figure 1](image-url)
Table 1 Weld parameters of the mockup

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The multi-pass weld beads have sharp transition angles, as shown in Figure 2, which demands extremely fine meshes. More importantly, the intersecting longitudinal and circumferential welds needs compatible meshing. Due to such complications, the weld bead was divided into small rectangle-shaped areas matching the experiment bead morphology as closely as possible. The experimental bead morphology of each pass is outlined by the dotted curves in Figure 2 and the corresponding simulation passes are highlighted in various colors. Such simplification avoided elements with sharp angles and assisted the FE model to converge more easily.

![Experimental bead morphology and the corresponding computational weld bead](image)

Figure 2. Experimental bead morphology and the corresponding computational weld bead

### 2.1.2 Material Properties

The mockup base material is 304 stainless steel (SS). The material properties used in the simulation were taken from Deng’s work [9], which is tabulated in Table 2. Temperature-dependent hardening modulus used in this model was obtained from Liu’s work [10]. The material solidus and liquidus temperatures were set at 1400 and 1450 °C, respectively. The latent heat of fusion was set to be 260 kJ/kg. The material properties were assumed to be the same for both base and weld metals due to lack of information in 308 weld metal physical properties.

### 2.1.3 Heat Source Model

Double-ellipsoidal heat source model developed by Goldak [11] as illustrated in Figure 3 was used to simulate the heat input of submerged-arc welding process. The front and rear parts of the heat flux are described by Eqs. (1) and (2), respectively:

\[
q_f(x, y, z) = \frac{6\sqrt{3}f_{x}\eta Q}{a_fbc\pi\sqrt{\pi}} \exp\left(-\frac{3x^2}{a_f^2} - \frac{3y^2}{b_f^2} - \frac{3z^2}{c^2}\right) \quad (1)
\]

\[
q_r(x, y, z) = \frac{6\sqrt{3}f_{x}\eta Q}{a_rbc\pi\sqrt{\pi}} \exp\left(-\frac{3x^2}{a_r^2} - \frac{3y^2}{b_r^2} - \frac{3z^2}{c^2}\right) \quad (2)
\]

where the front and rear quadrant fractions, \(f_f\) and \(f_r\), were set to be 0.6 and 1.4, respectively. The heat input was defined as \(Q=V*I*\eta\), where \(V=30\text{V}, I=400\text{A}\) and \(\eta=0.8\). \(a_f, a_r, b, c\) were set to be 13, 26, 13, 13, respectively, to closely match the experimental fusion boundary in Figure 2.
Figure 3: Heat source model used for weld simulation [11].

Table 2: Materials properties of 304SS used in the weld model

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<th>Specific heat (J/g·℃)</th>
<th>Conductivity (W/m·℃)</th>
<th>Density (g/mm³)</th>
<th>Yield stress (MPa)</th>
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2.2 Weld-Induced Residual Stress Simulation Results

2.2.1 Temperature Profiles in Weldments

The constants in Eqs. (1)-(2) were adjusted to match the fusion boundary of the experimental welds. The fusion zone generated from the three inner passes and four outer passes of the longitudinal welds were integrated to calculate an overall fusion boundary for the whole welding process as depicted in Figure 4.
Figure 4 Temperature contours of individual weld pass in the longitudinal welds: (a) inner passes, (b) outer passes, and (c) comparison of fusion boundary between simulation and experimental observation.

2.2.2 Residual Stress Contours

Figure 5 summarizes the overall stress contours in the mockup after seven longitudinal weld passes and eight circumferential weld passes. The thermal contraction during solidification and cooling of arc welding induced high tensile residual stress in the weld metals. In the longitudinal welds, as shown in Figure 5 (a), the axial stress is as high as 423.7 MPa in the weld center, which is much higher than the hoop stress. In comparison, a maximum residual stress of 366.1 MPa lies in hoop direction in the circumferential welds. The influence of two intersecting multi-pass weldments on the residual stress distribution is clearly demonstrated in Fig.5 as well. It should be noted that the highest tensile stress always coincided with the welding direction.
2.2.3 Residual Stress in Circumferential Welds

Figure 6 summarizes the residual stress profiles as a function of depth in circumferential weld centerline and HAZ (~4mm away from weld toe on the outer surface) obtained from FE analysis (FEA) and deep-hole drilling (DHD) measurements, which demonstrates a good agreement. Note that the experimental residual stress data close to the surfaces (≤2mm) were obtained from conventional hole drilling method. Through-wall high hoop tensile stress was observed in the circumferential welds. The maximum hoop stresses in circumferential welds are about 310 MPa in the weld centerline and 220 MPa in HAZ, respectively. The pre-existing residual stress in the base metal induced (up to 50MPa indicated by the DHD measurements) by the rolling process during manufacturing which was not considered in the FE model, may lead to the difference in residual stress values near surfaces between experimental and simulation results.
The cross-sectional stress contour is extracted from FEA results, and compared with the results from contour method for both circumferential and longitudinal weld. Figure 7 demonstrates the comparison of circumferential weld. Good agreement was achieved between the FEA and contour measurement results. The residual stresses are strongly tensile through wall near the weld centerline. Note that tensile stress is observed at the two ends of the welded plate in the contour method, as shown in Figure 7 (a), which could be potentially introduced by cutting process.

### 2.2.4 Residual Stress in Longitudinal Welds

Figure 8 compares the axial and hoop stress profiles in the longitudinal weld centerline and HAZ as a function of the thickness. Through wall high tensile axial stress is observed. The maximum axial stresses are around 420 MPa and 220 MPa for weld centerline and HAZ, respectively. The lower stress value on the surface from experimental measurements may be caused by the rolling process during manufacturing prior to welding.

Figure 9 compares the cross-sectional stress contours from FEA and contour measurement for longitudinal weld. FEA results agree well with contour measurement results. The tensile stress region extends approximately 25–30 mm away from the center of fusion zone for longitudinal weld case. The residual stresses are all tensile through thickness inside the weld. The simulation result predicts a slightly wider tensile residual stress region than the contour method, especially on the inner and outer surfaces, which is in better agreement with the experimentally observed fusion boundary morphology as illustrated in Figure 4.

![Figure 7: Cross-sectional hoop stress maps for circumferential weld from (a) contour method and (b) FE model.](image-url)
Figure 8: Residual stresses profiles in (a) weld centerline and (b) HAZ of longitudinal weld from FEA (dashed lines) and DHD measurements (solid lines). The data of FEA is averaged from ten points in the steady state location.

Figure 9: Cross-sectional axial stress contour distributions for longitudinal weld from (a) contour method and (b) FEA.

2.2 Sensitivity Study

The accuracy of the FE results depends on many factors, such as the material property inputs. Also, the welding parameters adopted by different manufacturers may vary slightly such as welding speed and welding direction in the construction of the canisters, which leads to potential differences in maximum stress levels and the resulting corrosion rates. Hence, a sensitivity analysis was performed to evaluate the influence of individual parameters on the simulation results.

For the sensitivity study, because the calculation of the whole model with intersecting joints is time-consuming, only the influence of material property database was considered using the whole model, and the data was collected in the steady state. For the other factors including welding direction and time interval between passes, the longitudinal multi-pass weld that introduced the highest residual stress was simulated, and the two red points in Figure 10 highlight the data collection locations as a function of thickness for
sensitivity analysis, with one located in the weld centerline and the other in HAZ. Table 3 summarizes the
variants used in the sensitivity study, i.e., material physical properties, and welding parameters including
welding direction and time interval between passes.

![Diagram of HAZ and Weld Centerline with Data Collection Sites]

Figure 10: Two data collection sites for the longitudinal weld in sensitive study.

Table 3: Variants matrix for the sensitivity study (Note: The data highlighted by underlines were those used
in the final mockup model.)

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2.2.1 Influence of Material Property Database

A total of four different groups of material properties for 304SS were selected to use in the model sensitivity
analysis. The material properties used in the model discussed above were from the work by Dean et al.
published in Computational Materials Science (CMS) [9]. The other three groups of material properties for
304SS are found in journals including Journal of Manufacturing Process (JMP) [12], Fusion Engineering
and Design (FED) [10], and U.S. NRC Technical Letter Report [8]. Note that the temperature-dependent
hardening modulus used in the final model was obtained from the publication by Liu et al. in FED [10].
The temperature-dependent material properties from these resources including Young’s modulus, thermal
expansion coefficient, specific heat, thermal conductivity, and yield stress are summarized in Figure 11-
Figure 14 and Table 4.
Figure 11: Temperature-dependent Young’s modulus from different material databases.

Figure 12: Temperature-dependent thermal expansion coefficient from different material databases.
Figure 13: Temperature-dependent specific heat from different material databases.

Figure 14: Temperature-dependent thermal conductivity from different material databases.
Table 4: Temperature-dependent yield stress.

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The hoop stress distributions on the outer surface in circumferential welds generated from the four groups of material properties are compared in Figure 15. It is observed that the maximum residual stress generated from NRC’s material input was extremely high (close to 946 MPa, near the middle thickness in fusion zone), while the CMS’s material input produced the lowest (~366 MPa) and widest tensile residual stress region. The maximum axial stress values using JMP’s and FED’s material properties were around 490 MPa.
and 580 MPa, respectively. Note that weld metal also used the base metal material database in the models discussed here.

Figure 16 summarizes the calculated hoop residual stress along the thickness direction in the weld centerline using the four groups of material properties in comparison to the DHD measurement result. It was observed that NRC data produced the overall highest hoop residual stresses, while CMS produced the lowest and matched the DHD measurement results the best. For the hoop residual stress as a function of thickness in the HAZ, the calculated stress values using the four groups of material properties showed a similar trend, as demonstrated in Figure 17. It is evidently shown that the calculations using CMS’s material properties matched the experimental measurement results reasonably well.

Figure 15: Axial stress distributions in longitudinal welds generated by material properties from different references: (a) CMS, (b) JMP, (c) FED and (d) NRC.

Figure 16: Hoop residual stress as a function of thickness in weld centerline generated by material properties from different references in comparison to the DHD measurement result.
2.2.2 Influence of Welding Direction

The welding direction during manufacturing of the mockup canister was kept the same for all the passes. To reveal the influence of welding direction, a back-and-forth welding method, meaning that the welding direction alternated between each pass, was used in the multi-pass longitudinal welds. Figure 18-Figure 20 indicate that the change in welding direction has little to no influence on the axial stress distributions in the weld and HAZ, which was potentially due to a short welding time of ~3 min for one pass and 30 min long time interval between passes.

Figure 18: Axial stress distributions in multi-pass longitudinal welds with (a) one-direction, and (b) back and forth welding processes.
Figure 19: Axial residual stresses as a function of thickness in the weld centerline using one-direction and back-and-forth welding methods.

Figure 20: Axial residual stresses as a function of thickness in HAZ using one-direction and back-and-forth welding methods.

2.2.3 Influence of Time Interval

As Section 2.2.5 indicated that the long waiting time between passes led to comparable residual stress levels to the back-and-forth welding process, it is worth to evaluate the sensitivity of residual stress to the welding time interval. Figure 21 summarizes the axial stress contours generated from five different time intervals, ranging from 15min to 35min, between welding passes. Negligible difference in the maximum stress levels and distribution patterns were observed. Figure 22 and Figure 23 further compared the residual stresses in details. A slight decrease in tensile residual stress was observed on the outer surface in the weldments. On the contrary, noticeable increase in the axial residual stresses in the HAZ throughout the wall was observed as the time interval was reduced from 35min to 15min. Therefore, a sufficient long time interval, >30min, is recommended for this mockup multi-pass welding process for the purpose of residual stress control.
Figure 21: Axial stress contours in longitudinal welds with different time intervals in-between passes.

Figure 22: Axial residual stress along the depth direction in the weld centerline with different time intervals in-between passes.
2.3 Influence of Gravity

The gravity of the canister and used-fuel was taken into consideration in the stress analysis. The weight of the canister was calculated to be 2,502 kg based on its geometry. The total weight of fuel inside the dry canister was estimated to be about 35,698 kg, assuming there were 24 assemblies in the canister and 17x17 fuel rods per assembly. The gravitational acceleration was set to be 9.8 m/s². Canisters in both vertical and horizontal positions were simulated. For the vertical type, the bottom surface of the canister was fixed, and the gravity was along the axial direction of canister, as seen in Figure 24(a). For the horizontal canister, three surfaces with a dimension of 20 mm in width (parallel to longitudinal direction of the canister) and a curvature of 45° was fixed to support the weight, as shown in Figure 24(b) and the gravity was perpendicular to the axial direction. The geometry of the two canisters was the same as what was used in Figure 1. The fuel bars in the canister were simplified as a point mass located in the center of canister with a weight of 35,698 kg. This point mass was coupled to the canister with 4 points at the top, middle and bottom, respectively, as illustrated in Figure 24(c). The models were meshed using 66,300 brick elements. Note that this stress analysis focused on the influence of gravity only, and the weldments were not included.
Figure 24: Geometry of the canisters in (a) vertical and (b) horizontal positions and the (c) coupling between point mass and canister.

The stress distributions along the principal directions in the canister in vertical position under gravity is shown in Figure 25. It was observed that gravity of the canister and used-fuels induced stress concentration at the bottom inner surface of the canister. Hoop stress exhibited a maximum value of 45MPa, as shown in Figure 25 (b). The stresses were generally negligible on the outer surface, i.e., less than 3MPa along all the three principal directions. Within the canister in horizontal position, gravity also led to stress concentration on the inner surfaces where the support structures were located at, as shown in Figure 26. Axial stress exhibited a maximum value of about 58MPa. The stresses were generally less than 5 MPa along the three principal directions on the outer surface, which is negligible in comparison to the weld induced residual stresses. In summary, the gravity of the canister and used-fuels induced negligible stresses on the outer surface of the canisters of vertical and horizontal types. It is recommended to avoid overlapping the supporting locations with welding seams though.
3. REPLICATION OF RESIDUAL STRESSES

The stresses experienced by the mockup materials were duplicated to laboratory scale specimens through four-point bending (FPB) test. Two types of FPB setups were used, including a large modified setup and a small conventional one. The modified FPB setup was designed to reveal the effects of stress on pitting/cracking initiation and growth in a single specimen, for the purpose of minimizing uncertainties. The conventional small FPB setup was designed for field test since the limited space between the spent fuel canister and overpack does not allow for the placement of many large-sized modified FPB setups.
3.1 Modified Four-Point Bending Setup

Conventionally, such as in ASTM D6272-10, examinations on a FPB specimen are made within a constant load span. On the contrary, in this modified FPB setup, pitting initiation/growth was characterized within the colored region in Figure 27 (a), which covered stress levels from compression to tension. The specimen geometry was designed using FE method, to allow for a sufficient sampling area within a small stress increment. Digital image correlation (DIC) method was used to validate the geometry design.

The base metal FPB specimens were cut along the transverse direction (TD) of the base metal plates (including 304L and 304H stainless steels) as indicated in Figure 27 (a). The reason for such a cutting direction is that the maximum residual stress in the mockup longitudinal welds was observed along axial direction as illustrated in Figure 28, i.e., normal to the rolling direction (RD) in Figure 27(b). Therefore, the FPB specimens were machined along TD of the base metal plates to simulate the actual loading condition on the rolling microstructure of the mockup. The weldment FPB specimens were cut across the mockup longitudinal welds instead, to further reveal the influence of microstructure variation across the weld on pitting/cracking initiation and growth.

![Figure 27: (a) A modified four-point bending setup with the sampling area highlighted by green and red colors. The red color indicates tensile stress region, while the green color indicates compressive stress region. The plate in gray represents the base metal. TD, RD and ND stand for transverse, rolling and normal directions, respectively. (b) Schematic drawing of the mockup with three longitudinal and two circumferential multi-pass welds.](image)
3.1.1 Geometry Design

FEA was performed to design the geometry of the FPB specimen and loading frame. Different thicknesses and widths of the loading frame were analyzed to ensure low stress concentration while minimizing waste of materials. Figure 29 illustrates the finalized the geometry design. The total length and height of the loading frame is 420 mm and 126.5 mm, respectively, which can easily fit in the humidity chamber. The FPB specimen has a dimension of 16.5 × 15.9 × 320 mm³. 15.9mm is the original thickness of 304 stainless steel plates. Figure 30 shows the Von Mises stress distribution in the modified FPB setup with a maximum load of 217 MPa. The stress concentration near the frame inner corners is negligible. The frame material is 316 stainless steel. The frames were coated with Kolor-Proxy high build polyamide-epoxy primer that provides abrasion, impact and chemical resistance. More importantly, the coatings prevent formation of galvanic couples at the contact point between the loading frames and specimens.

Digital image correlation (DIC) method was used to in-situ monitor the strain development in the designed FPB setup during incremental loading for the purpose of validation. Figure 31 (a) shows the DIC measurement setup. Figure 31 (b) demonstrates the surface preparation for DIC measurement, where a white background and black speckle pattern was generated by carefully spraying the white coating primer and low chloride metal marker black paint. The reason for the selected primer and paint is because these loaded FPB specimens were later sent to Maine Yankee for field testing. The two screws in Figure 31 (b) were used to slowly apply loads, and the induced strain was recorded by DIC.
Figure 29: Optimized geometry of the modified FPB setup by FEA.

Figure 30: Von Mises stress distribution in the optimized FPB setup.

Figure 31: (a) Photograph of the DIC setup for FPB testing, and (b) the speckle pattern on the side surface of FPB setup prepared for DIC analysis.
Figure 32(a) presents the stress distribution in half of the 304 specimens obtained from FEA, where S11 refers to principal stress along X axis. A downward displacement of 1.08 mm was applied in the center of the specimen by turning the two screws simultaneously, which induces a maximum X-stress of 217 MPa. Note that a higher stress matching the maximum residual stress observed in mockup model was applied in the actual experiments on SCC behavior examination. Figure 32 (b) and (c) demonstrate how the X-stress varied along normal direction (ND) and distance away from the centerline on the bottom surface, respectively. Using this modified FPB setup, within a stress span of ±25MPa on its side surface, the sampling area for SCC behavior is as large as 2mm in height and 120mm in length, as highlighted by the red areas in Figure 32 (b) and (c).

Figure 32: Stress profiles of the modified FPB specimen with a displacement load of 1.08 mm: (a) on the ND-LD half side surface; (b) along ND at the center of the specimen; and (c) along LD on the bottom surface starting from the center of the specimen. ND and LD denote normal and longitudinal directions, respectively.

DIC method was able to provide the strain evolution along x axis (//LD) as a function of displacement load along y axis (//ND) in a modified FPB specimen as summarized in Figure 33. The displacement load was carefully applied by turning the two screws in Figure 31 (b) downward slowly and evenly. Good agreement was achieved between the strain profiles obtained from DIC measurement and FEA, as plotted in Figure 34.
Figure 33: Strain evolution along x axis (longitudinal direction) on the side surface of a modified FPB specimen as a function of displacement load along y axis

Figure 34: Comparison of strain contours obtained from (a) FEA and (b) DIC measurement on the modified FPB specimen, and (c) the strain variations as a function of depth from top surface in the center of the specimen subtracted from the strain maps in (a) and (b).

3.1.2 Influence of Environmental Temperature on Load Conditions

The modified FPB specimens are planned to be placed in humidity chambers at various temperature conditions. Therefore, how the environmental temperature affects the FPB load condition needs to be evaluated. As compared in left column of Figure 35, the maximum stress on the specimens with a displacement loading of 1.08 mm gradually decreased from 217 MPa to 174 MPa as the temperature
increased from 20 to 80 °C. To maintain a constant stress level of 217MPa, the displacement load needed to be adjusted to 1.15mm and 1.26 mm for an environmental temperature of 40°C and 80°C, respectively, as summarized in the right column of Figure 35.

![Displacement load at different temperatures](image)

Figure 35: Effect of temperature (ranging from 20 to 80°C) on FPB loading conditions (on the left) and the required adjustment of displacement load to maintain a constant loading condition (on the right).

### 3.1.3 Modified FPB Specimens Loaded for SCC Examination

A total of 17 specimens have been loaded using the modified FPB setup for both laboratory scale examination in a humidity chamber and field test at Maine Yankee. The maximum stress level loaded on the FPB specimens was 250MPa, matching the as-welded stress condition in the heat affected zone of canister weldments. Based on the analysis in section 3.1.2, stress change in the FPB specimens is expected after exposure to various environmental temperatures. In other words, the 17 specimens placed at different testing sites and environments would experience various levels of stress relaxation. The FPB specimens were machine from three different materials, including Type 304L and 304H stainless steel plates, and a piece of mockup canister wall containing both longitudinal and circumferential weldments.

It is noted that occasionally finish grinding is used in welding techniques for various purposes, such as to provide a flat surface for ultrasonic inspection, to clean slags trapped in weld bead, or to correct excessive convexity which serves as a stress riser. Such uncertainty leads to the needs for evaluating the effects of surface roughness on SCC behavior. Therefore, for specimens machined from Type 304L and 304H stainless steel plates, three surface conditions were used, including the as-received mill finish, ground with 36# grit, and mirror-polish, in order to evaluate the influence of surface roughness. The loaded FPB specimen with a circumferential weld located in the center in the as-received condition is demonstrated in Figure 36. The whole loading frame and the top and bottom surfaces of the specimen were coated with Kolor-Proxy high build polyamide-epoxy primer to prevent formation of galvanic couples at the contact point.

For field test, eight loaded specimens were placed in four storage casks at Maine Yankee including two under hotter and two under cooler temperature conditions. The specimens were placed at the inlet or outlets facing the prevailing wind or on the back side of the casks with wind being blocked. The conditions are tabulated in Table 5.
Figure 36 Photograph of a modified FPB setup with a mockup specimen containing a multi-pass circumferential weld located in the center.

Table 5 Conditions of large modified FPB specimens for field test at Maine Yankee

<table>
<thead>
<tr>
<th>Tag number</th>
<th>Materials</th>
<th>Surface Condition</th>
<th>Max. Stress (MPa)</th>
<th>Weld Type</th>
<th>Location Info.</th>
<th>Start date (m/d/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>304L</td>
<td>Mill</td>
<td>250</td>
<td>BM</td>
<td>MY#I#H#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L4</td>
<td>304L</td>
<td>36# grit</td>
<td>250</td>
<td>BM</td>
<td>MY#I#C#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L6</td>
<td>304H</td>
<td>Polished</td>
<td>250</td>
<td>BM</td>
<td>MY#O#C#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L14</td>
<td>304L</td>
<td>Mill</td>
<td>250</td>
<td>BM</td>
<td>MY#O#H#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L15</td>
<td>304L</td>
<td>36# grit</td>
<td>250</td>
<td>BM</td>
<td>MY#O#C#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L16</td>
<td>304L</td>
<td>Polished</td>
<td>250</td>
<td>BM</td>
<td>MY#O#H#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L18</td>
<td>Mockup</td>
<td>As-received</td>
<td>250</td>
<td>CW</td>
<td>MY#I#H#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>L19</td>
<td>Mockup</td>
<td>As-received</td>
<td>250</td>
<td>LW</td>
<td>MY#I#C#B</td>
<td>9/1/17</td>
</tr>
</tbody>
</table>

Note: BM – Base Metal; CW - Circumferential Weld; LW - Longitudinal Weld; MY - Maine Yankee; I - Inlet; O - Outlet; H - Hot; C - Cool; B - Blocked wind; P - Prevailing wind.

For laboratory scale test, different amount of salt was deposited on the side surface of the loaded specimens, i.e., the front surface in Figure 36. Before salt deposition, the sample was preheated to 50°C for 30min in a drying chamber with 0% relative humidity. Then it was placed in a deposition chamber, and a humidifier nozzle was secured on top of the chamber to spray ASTM D1141-98 seawater mist. The specimens were taken out every 5min and placed in a drying chamber for 3min, until desired deposition density was achieved. Six small test coupons with an area size of 5×5cm² were used to monitor the amount of salt deposited on the FPB specimen surface. For instance, one small coupon was taken out every 10min. The salt deposited on top surface was dissolved first in 250mL DI water for conductivity measurement. Two different salt loads were applied, including 2 and 4 g/m², as shown in Figure 37. A total of nine specimens were placed in a humidity chamber at CSM simulating a relative humidity of 35% and an environmental temperature of 50°C. The testing conditions are summarized in
Table 6.

Figure 37 SEM images of salt distributions on the small test coupons with a salt load of 2 g/m² and 4 g/m², respectively.
### Table 6 Conditions of large modified FPB specimens for laboratory scale test

<table>
<thead>
<tr>
<th>Tag number</th>
<th>Materials</th>
<th>Surface Condition</th>
<th>Max. Stress (MPa)</th>
<th>Weld Type</th>
<th>Location and HCN#</th>
<th>Salt Load (g/m²)</th>
<th>Start date (m/d/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L2</td>
<td>304H</td>
<td>Mill</td>
<td>250</td>
<td>BM</td>
<td>CSM2</td>
<td>4</td>
<td>8/9/17</td>
</tr>
<tr>
<td>L3</td>
<td>304L</td>
<td>Polished</td>
<td>250</td>
<td>BM</td>
<td>CSM2</td>
<td>4</td>
<td>8/9/17</td>
</tr>
<tr>
<td>L5</td>
<td>304L</td>
<td>Mill</td>
<td>250</td>
<td>BM</td>
<td>CSM2</td>
<td>4</td>
<td>8/8/17</td>
</tr>
<tr>
<td>L8</td>
<td>304L</td>
<td>36# grit</td>
<td>250</td>
<td>BM</td>
<td>CSM2</td>
<td>4</td>
<td>8/3/17</td>
</tr>
<tr>
<td>L9</td>
<td>Mockup</td>
<td>As-received</td>
<td>250</td>
<td>CW</td>
<td>CSM2</td>
<td>2</td>
<td>8/3/17</td>
</tr>
<tr>
<td>L10</td>
<td>Mockup</td>
<td>As-received</td>
<td>250</td>
<td>CW</td>
<td>CSM2</td>
<td>4</td>
<td>8/1/17</td>
</tr>
<tr>
<td>L12</td>
<td>304H</td>
<td>36# grit</td>
<td>250</td>
<td>BM</td>
<td>CSM2</td>
<td>2</td>
<td>8/8/17</td>
</tr>
<tr>
<td>L13</td>
<td>Mockup</td>
<td>As-received</td>
<td>250</td>
<td>LW</td>
<td>CSM2</td>
<td>4</td>
<td>8/2/17</td>
</tr>
<tr>
<td>L17</td>
<td>304H</td>
<td>36# grit</td>
<td>250</td>
<td>BM</td>
<td>CSM2</td>
<td>4</td>
<td>8/3/17</td>
</tr>
</tbody>
</table>

Note: HCN# - Humidity Chamber Number; CSM1,2 – Humidity chambers Number 1 and 2 located at CSM.

#### 3.2 Conventional Four-Point Bending Setup

Besides the modified four-point bending samples mentioned above, smaller sized conventional FPB specimens were also prepared for field test. The corrosion behavior study will be performed on the surface with a constant stress span. The geometry of the small conventional FPB setup was optimized from FEA, which is shown in Figure 38. The samples were all machined from Type 304L stainless steel base metal plate. Four different surface conodonts including the as-received mill finish, ground with 36# grit and 60# grit, and mirror-polish, in order to evaluate the influence of surface roughness in pitting/cracking initiation and growth. Three maximum stress levels, 310 MPa, 240 MPa and 150 MPa were applied to specimens to reveal the effects of stress level on SCC behavior. DIC testing in combination with the FEA was used to achieve the desired maximum load level, following the same procedures described in section 3.1.1. Testing conditions of the 24 small conventional samples are summarized in Table 7.

![Figure 38: Geometry design and dimensions for the mini four-point bending setup.](image)
Table 7 Conditions of the small conventional FPB specimens for field test at Maine Yankee

<table>
<thead>
<tr>
<th>Tag number</th>
<th>Materials</th>
<th>Surface Condition</th>
<th>Max. Stress (MPa)</th>
<th>Location Info.</th>
<th>Start date (m/d/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>304L</td>
<td>36#</td>
<td>310</td>
<td>MY#I#H#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S2</td>
<td>304L</td>
<td>60#</td>
<td>310</td>
<td>MY#I#C#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S3</td>
<td>304L</td>
<td>Polished</td>
<td>310</td>
<td>MY#I#C#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S4</td>
<td>304L</td>
<td>Mill</td>
<td>240</td>
<td>MY#I#H#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S5</td>
<td>304L</td>
<td>60#</td>
<td>240</td>
<td>MY#I#C#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S6</td>
<td>304L</td>
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</tr>
<tr>
<td>S7</td>
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<td>150</td>
<td>MY#I#C#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S8</td>
<td>304L</td>
<td>Mill</td>
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</tr>
<tr>
<td>S9</td>
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<td>Mill</td>
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</tr>
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<tr>
<td>S11</td>
<td>304L</td>
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<td>S12</td>
<td>304L</td>
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<tr>
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<td>9/1/17</td>
</tr>
<tr>
<td>S15</td>
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<td>240</td>
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</tr>
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</tr>
<tr>
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<td>304L</td>
<td>60#</td>
<td>240</td>
<td>MY#O#C#B</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S18</td>
<td>304L</td>
<td>Polished</td>
<td>150</td>
<td>MY#I#C#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S19</td>
<td>304L</td>
<td>Polished</td>
<td>150</td>
<td>MY#O#C#P</td>
<td>9/1/17</td>
</tr>
<tr>
<td>S20</td>
<td>304L</td>
<td>36#</td>
<td>150</td>
<td>MY#I#H#P</td>
<td>9/1/17</td>
</tr>
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<td>MY#O#H#P</td>
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</tr>
<tr>
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<td>150</td>
<td>MY#O#C#B</td>
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</tr>
<tr>
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<td>Mill</td>
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</tr>
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<td>Mill</td>
<td>310</td>
<td>MY#O#H#B</td>
<td>9/1/17</td>
</tr>
</tbody>
</table>

4. FEA of Pit-to-Crack Transition

The existence of pit tends to intensify the local stress field and thus increases the stress intensity factor. Pit-to-crack transition occurs as the stress intensity factor is greater than the critical value. Therefore, the effect of pit morphology on stress redistribution was analyzed by FE modeling in this section using four different types of theoretical pit shapes based on literature survey. Future examination of the corrosion attack morphology on the FPB specimens described in Section 3.1.3 will provide the database of real pit morphologies for a more realistic analysis of the pit-to-crack transition in the Canister materials.
4.1 Pit Modeling

Four types of pits with different morphologies, i.e. hemi ellipsoidal, partial spherical, U-shaped and V-shaped, were used in the 3D FE model, as illustrated in Figure 39. For the partial spherical case, the pit shape is marked by the shaded area. For the other three cases, the pit morphologies are just as sketched. The geometrical parameters of each pit shape including pit depth and opening width were varied in the FEA. The depth of pit was varied from 100µm to 10mm, and the opening diameter of pit from 250µm to 2mm. Different aspect ratio (a/2c or h/2c) were used to identify its effect on stress redistribution. The effects were quantified by a stress concentration factor (SCF), which is defined as the ratio of the highest stress to the nominal applied stress. The geometry of the substrate plate used in this analysis was the same as the mockup residual stress model described in Section 2.1 Figure 1, except that the welds were not included in this model. Due to the geometrical symmetry of the canister, one quarter of the cylinder was simulated with a quadrant of a pit located at its right top corner on the outer surface. Figure 40 illustrates the models with four different pit morphologies meshed using around 150,000 10-node quadratic tetrahedron elements. In order to accurately predict the stress and strain while saving the simulation time, the mesh was only refined near the pits. A uniaxial tension stress of 250 MPa was applied along axial direction on the canister, simulating the maximum residual stress of 250MPa presented in the HAZ of canister mockup, as presented in Section 2.2. The cross-sectional area of pits was neglected in the calculation of nominal tension stress, due to their small size in comparison to the substrate plate.

![Figure 39: 3D geometrical illustrations of four different types of pits.](image)
4.2 Effect of Pit Morphology on Stress Concentration Factor

In order to reveal the influence of pit geometry parameters on stress concentration, pits with different opening diameter and depth were simulated. First of all, as summarized in Table 8, for each pit type, three sets of pit diameter and depth that generate the same geometry aspect ratio (a/2c or h/2c) were used in the FE models to calculate the corresponding SCF values. It was found that for each pit type, as the aspect ratio was kept constant, the calculated SCF were approximately constant. In other words, the pit aspect ratio (a/2c or h/2c) is the main parameter controlling stress concentration in pitting corrosion \[13\]. Therefore, in the following calculations, the pit aspect ratio was varied in a wide range (i.e., 0~24) to elucidate its influence on SCF.

Table 8: SCF values of pits with different mouth width and depth.

<table>
<thead>
<tr>
<th>Pit Morphology</th>
<th>a (mm)</th>
<th>2c (mm)</th>
<th>h (mm)</th>
<th>a/2c</th>
<th>h/2c</th>
<th>SCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>0.5</td>
<td>2</td>
<td>0.25</td>
<td></td>
<td></td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.2</td>
<td>0.25</td>
<td></td>
<td></td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>0.25</td>
<td></td>
<td></td>
<td>1.22</td>
</tr>
<tr>
<td>Type 2</td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td></td>
<td></td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1.2</td>
<td>0.5</td>
<td></td>
<td></td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.8</td>
<td>0.5</td>
<td></td>
<td></td>
<td>1.33</td>
</tr>
<tr>
<td>Type 3</td>
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<td>1</td>
<td>1</td>
<td></td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.6</td>
<td>1</td>
<td></td>
<td></td>
<td>1.4</td>
</tr>
</tbody>
</table>
Figure 41 summarizes for each pit type how the value of SCF changes as a function of the aspect ratio (a/2c or h/2c). In the hemi-ellipsoidal shaped and U-shaped pits, SCF value raised rapidly with the aspect ratio at lower value range and the slope decreased drastically as the aspect ratio increased. Under the partial spherical case, the SCF and a/2c relation followed y=Ax^2 curve, in which the maximum SCF value occurs when a is equal to c, i.e., in the case of a hemi-spherical shape. For the V-shaped pit type in Figure 41(d), the SCF value increased quickly as a/2c was below 1.0. As the aspect ratio further increased, the SCF value maintained at about 2.2. There were slight fluctuations in SCF between an aspect ratio of 2-3. The reason for the fluctuation was most likely caused by the difficulties associated with meshing the sharp corner in the V-shaped pit.

<table>
<thead>
<tr>
<th></th>
<th>0.4</th>
<th>0.4</th>
<th>1</th>
<th>1.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 4</td>
<td>0.4</td>
<td>0.8</td>
<td>0.5</td>
<td>2.52</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1.2</td>
<td>0.5</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>0.5</td>
<td>2.56</td>
</tr>
</tbody>
</table>

Figure 41: Variations of SCF for each type of pit: (a) Hemi-ellipsoidal, (b) partial-spherical, (c) U-shaped and (d) V-shaped
4.3 Local Stress and Strain Redistribution

Figure 42-Figure 45 compare the contour maps of principal maximum stress and plastic strain calculated from the four pit morphology types. It was observed that the geometry parameter variation in each pit type did not affect the overall patterns of the contour maps of the principal maximum stress and plastic strain. As shown in Figures 45-47, as the bottom surfaces of the pits were smooth and contained a reasonably large radius, maximum plastic strain accumulated near the shoulder of the pits while the maximum principal stress concentrated near the bottom of the pits. In comparison, in the V-shaped pit, as shown in Figure 45, both the maximum stress and plastic strain was present at the bottom sharp tip. Such difference indicates that cracking initiation location greatly depends on the pit morphology. For instance, Horner et al. [14] examined the evolution of stress corrosion cracks from corrosion pits in turbine disc steels exposed to simulated steam-condensate and found crack initiating near the shoulder of the U-shaped and hemispherical shaped pits. On the other hand, for a Type 4 pit with a V-shape, crack will most likely initiate at the bottom sharp tip. It should be noted that the pit-to-crack transition is determined by both the local mechanics and local chemical activity within the pit. The results here just demonstrate the important role of local mechanics. These results can be as a reference when analyzing the initiation of cracks on the canister in future studies.

Figure 42: Maximum principal stress and strain distribution for a hemi-ellipsoidal pit with 0.5 mm opening width and 1 mm depth.

Figure 43: Maximum principal stress and strain distribution for a partial spherical pit with 0.6 mm opening width and 0.6 mm depth.
5. FEA of Pre-Cracked Tensile Specimens for In-Situ SCC Experiment

Our collaborators from North Caroline State University performed in-situ SCC experiment using high-energy X-ray tomography and diffraction in 1-ID beam line of the Advanced Photon Source (APS) at Argonne National Laboratory to evaluate the crack initiation and growth in pre-cracked tensile specimens including 304, 304H and 304L stainless steels. The experiment setup and specimen geometry are shown in Figure 46. The pre-cracked specimens had a dimension of $1.15 \times 1.15 \times 35$ mm$^3$ and the crack with a depth of 550µm and opening of 100µm was located in the middle of the specimens. The temperature within the environmental cell was set at 70-80°C and the relative humidity was about 55-65%. The specimens were under a corrosive environment ($\text{MgCl}_2$, 50g/100ml) and uniaxial tensile loading condition, i.e., a maximum load of 206N for 304L, 260N for 304, and 288N for 304H. FEA was performed on the 304 and 304L specimens to provide the stress and strain distributions around the pre-existing crack tip, which is critical for understanding the crack propagation behavior that is currently under analysis. The model was meshed with brick elements with a fine mesh size in the region close to the crack, as shown in Figure 46 (b). A total of 136242 elements were meshed. The material properties used in the model were the same as the weld residual stress simulation model for 304 stainless steel as described in Section 2.1.2.
Figure 47 and Figure 48 demonstrate the calculated maximum principal stress and strain distributions under a tensile load of 206 N and 260 N, respectively. It can be seen that as the tensile load increased from 206 N to 266 N, the area exceeding a maximum principal stress of 500 MPa significantly broadened from a small spot in front of the crack tip in Figure 47 (a) to a butterfly-shaped region in Figure 48 (a). The total maximum principal strain exceeding 10% under the 206 N tensile load in Figure 47 (b) was close to a short vertical line on the crack tip. As the force load increased to 260 N, the strain field exceeding 10% evolved toward +45° and -45° directions in front of the crack tip. The FEA results indicate that significantly different corrosion cracking behavior would be expected from the two sets of experiments.

Figure 46 (a) Setup for in-situ SCC experiment at beam line 1-ID at APS, and (b) meshed model for the pre-cracked tensile specimen
In this SCC experiment, the fracture criteria would be $J$ integral exceeding the critical value $J_{1C}$ since the stainless steel materials are expected to experience both elastic and plastic deformation. In-situ x-ray tomography examination revealed obvious crack propagation initiated at the crack front of the 304 stainless steel sample under a load level of 260N after an exposure time of 3.1hr, while no crack growth was observed in the 304L specimen loaded under 206N after 13.8 hours. FEA using the domain integral method was...
performed to identify their corresponding J integral values for the prediction of $J_{1c}$ range related to this corrosion environment.

In this model, 20-node hexahedron elements with reduced integration points were employed in the contour integral regions, and the elements within the first contour domain surrounding the crack tip were converted to collapsed hexahedral elements, as shown in Figure 49 (a). Figure 49 (b) compares the calculated $J_1$ value as a function of contour domain number. In each specimen, the $J_1$ value approached a saturation value as the contour domain number increased, which was taken as the best approximation. For the 304L specimen under a load of 206N, $J_1$ was approximately 0.1972 mJ/mm², while for 304 specimen under a load of 260N, $J_1$ was about 0.3339 mJ/mm². It indicates that the critical value for J integral should be in between these two values, i.e., $0.1972 \text{ mJ/mm}^2 < J_{1c} < 0.3339 \text{ mJ/mm}^2$.

![Figure 49 Calculated J integral values as a function of contour domain number for 304L stainless steel under a load of 206N and 304 under a load of 260N](image)

6. Conclusions/Milestones

1) FE models were built for the intersecting double-V-groove multi-pass longitudinal and circumferential welds in a canister mockup. Good agreement in molten pool boundary was obtained between the modeling and experimental observation.

2) Welding-induced residual stresses from simulation were in good agreement with the experimental measurement results by deep-hole drilling and contour methods. Through-wall high tensile axial and hoop stresses were observed in both the fusion zone and HAZ in the longitudinal and circumferential weld, respectively.

3) The weight of the canister and fuels was found to have negligible influence on the residual stress distribution on the outer surface of the canisters.

4) Sensitivity analysis was performed to reveal the effects of material properties and welding parameters on the calculated residual stress contours. The material properties played an essential role in predicting the residual stress distribution. The welding time intervals affected the residual stress in HAZ more significantly than in fusion zone.
5) Modified and conventional FPB specimens were designed and prepared for duplication of mockup residual stresses to laboratory scale test of SCC behavior and field test at Maine Yankee.
6) The stress concentration factors induced by pitting with four different morphologies in the canister mockup were analyzed using FE models.
7) FEA of the pre-cracked tensile specimens for in-situ SCC experiment immersed in the MgCl₂ solution was performed and the J₁C value was preliminarily estimated.

7. Future Work

1) Corrosion damage morphology characterization on the modified FPB specimens will be performed to examine the pit morphology as a function of stress level, which will provide inputs for FE modeling of pit-to-crack transition.
2) More modified FPB specimens will be prepared for characterization of pit/crack growth rate.
3) Metallurgical characterization will be performed on SCC specimens to identify pitting initiation site.
4) Stress intensity factor distribution in the pre-cracked specimens will be analyzed and correlated to the in-situ SCC experiment results to identify the threshold stress intensity factor value.
5) A multiphysics finite element (FE) model will be developed to predict the crack growth rate in type 304 stainless steel canister weldments.

8. Reference


8. Appendix

Typical graphical user interface for the parameters setting in ABAQUS
Chapter 6
Chloride Detection and Life Prediction of Dry Storage Casks Using PGAA and NAA Techniques

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I. Abstract

Multiple barriers are used in dry storage casks to retain the nuclear fission products. Dust and aerosols in the air drawing through ventilation openings of the overpack may be deposited on canister surfaces. Under certain conditions, localized pitting leads to SCC. The aggressive chloride concentration that exists in marine environments can break the oxide protecting film, inducing pitting initiation\growth rate. Knowing the chloride traces\concentration at the canister surface is important for risk based inspection management. The non-destructive method based on prompt gamma-ray activation analysis (PGAA) and neutron activation analysis (NAA) of delayed gamma rays from radioactive daughter, resulting from neutron sources inside the canister, can be used to identify\quantify chloride. The intensities of the characteristic gamma peaks of chloride reveal their concentrations. The details of an analytical method employed to determine minimum detectable concentrations, including the capturing of gamma peaks of Na\Mg presented in salty environments, on the surface of a concrete overpack shielding system will be presented in this report.

In this effort, an assessment of a chloride detection method is performed for inspecting the surfaces of dry cask storage system (DCSS) canisters, with focus on the implementation of an NDE methodology. Some DCSS canisters (especially those located in coastal environments) will be exposed to environmental conditions, which can cause atmospheric stress corrosion cracking (SCC). Chloride deposits on canister surfaces provide the corrosive environment necessary for atmospheric SCC while residual stresses in weld regions or caused by cold work may provide the necessary driving force for crack growth. The heat-affected zones (HAZs) near welds are potentially susceptible to atmospheric SCC due to sensitization of the material caused by chromium depletion during the welding process. In addition, crevice conditions may contribute to canister degradation by trapping chloride deposits on the surface of the canister. Information collected from the field and from laboratory studies has not been able to rule out the possibility of atmospheric chloride induced stress corrosion cracking (CISCC), although no occurrences of atmospheric SCC in DCSS canisters have been detected. In this report, the results of a neutron activation analysis (NAA) and prompt photon activation analysis (PGAA) employing MCNP6, a highly sophisticated multi-physics code, are provided as an inspection methodology for inspecting dry storage canister surfaces. The gamma detection results are documented and summarized to quantitatively estimate the amount of chloride present on the surface of a canister as a function of gamma counts for particular energies that are signature of chloride in sea-salt. Sodium and magnesium, constituents of sea-salt, are also inspected for support and confirmation of chloride.
II. Introduction

Stress corrosion cracking (SCC) of interim storage containers has been indicated as a high priority data gap by DOE (Hanson, 2012), EPRI (2011), NWTRB (Rigby, 2010), and the NRC (2012, 2012a). Uncertainties exist both in terms of the environmental conditions that exist on the surface of the storage containers and the electrochemical properties of the storage containers themselves. The goal of this task is to assess the effects of environmental processes on canister performance, namely chloride deliquescence in marine environments, by evaluating the properties of a full-scale interim storage canister model. This model has been produced using the same manufacturing geometries and fuel loadings as fielded spent nuclear fuel interim storage canisters.

Engineering analysis of SCC susceptibility involves an assessment of materials, environment, and mechanical loading conditions. For SCC to occur, three factors must be present: a susceptible material, corrosive environment, and tensile loading conditions. This report is interested in the former two: atmospheric SCC in DCSSs is induced by chloride contamination on the outer surface of components in marine or coastal environments.

A portion of most atmospheric dusts consists of soluble salts. While the fraction of soluble salts in the particulates can be very small at locations far inland, for coastal locations, such as many interim storage sites, the fraction may be large. These salts may deliquesce to form brines on the surface of a storage container at temperatures well above the boiling point of water, and the resulting brines might be corrosive depending on the material used to construct the package. Stress corrosion cracking (SCC) of heat-affected zones near welds is of special concern, as it a well-documented mode of attack for austenitic stainless steels (including 304SS and 316SS) in marine environments (Kain 1990). A number of researchers have demonstrated that localized corrosion can take place under such situations on materials commonly used for interim storage containers, including 304SS (Cook et al. 2010; Shirai et al. 2011) and 316SS (Tani et al. 2009).

An assessment of a non-destructive chloride detection technique for inspecting the surfaces of spent fuel canisters is necessary to support the efficacy and functionality of an experimental field test. Also, the data gathered and delivered herein are vital in supporting a correlated CISCC analysis across multiple scientific fields within the materials research arena. There has become an increased reliance on computational methods that have been experimentally verified and validated. MCNP6 is the chosen code used in this study for modeling and simulating a fuel storage system.

Reviewing the literature on the amount of salt deposition from various experiments, the deposited salt load varies widely, sometimes orders of magnitude, from a few mg/m² up to hundreds of mg/m² over a wide range of time scales (from days up to years), depending on the site and the experimental design. Therefore, one nondestructive innovative technique that will be considered in this study is to make use of neutron activation techniques, which are very sensitive to the small quantities of material, to identify the presence, concentration and location of chlorine on the canister surface.

The flowchart below (Figure 1) displays the CISCC research project along the developmental path, with employment of inspection tools to assess a canister’s structural integrity, delineating how the project research study will develop and how inspection tools will be used to assess the structural integrity of spent fuel storage canisters due to CISCC that can allow independent spent fuel storage installation facilities (ISFSIFs) to manage the material degradation and inspections until repairs can be undertaken at a more economical or otherwise suitable time.
This figure captures both the spatial as well as the time-based variability of the corrosion degradation process at canister surfaces in order to be able to quantify the benefit of inspection coverage as well as inspection frequency. Inspections of the canister represent a highly efficient means of corrosion control and risk reduction of nuclear spent fuel storage. Quantitative corrosion models may form the basis for determining the optimal inspection efforts and economical time (i.e., what to inspect, when to inspect, and how to inspect). Such inspection planning procedures are based on the application of Bayes’ rule to update the uncertain corrosion model using inspection results, due to changes in the chemical and physical characteristics of the material and stress with depth and time. This variability is not explicitly modeled prior to inspection, increasing the scatter in observations, and should be accounted for by the statistical uncertainty model of the corrosion process. Time-based variability due to the inherent characteristics of the corrosion process will therefore be modeled by means of time-invariant random variables. On the other hand, the influencing environmental, material and stress parameters, which in experiments are generally held constant, often vary significantly with time due to the operational conditions of ISFSIs. Future degradation may be different from past degradation, and as such this time-based variability will be addressed in our proposed models. Information obtained from an onsite inspection will be used to update all random variables, which will then be applied for the prediction of future canister deterioration.

Since the corrosion process is non-linear in time, it’s very difficult to replicate the corrosion that occurs under actual field conditions at site in laboratory experiments. A more useful approach for risk based inspections of dry storage casks is to develop predictive models based on corrosion science modeling, materials properties and atmospheric marine environments with good quality field data, that will update the future prediction of canister degradation and the measured action need to be taken as indicated the above flowchart.
Figure 1. Flowchart of CISCC Analysis.
With laboratory supported experiments the proposed inspection tools will improve:

- Future performance predictions of canisters under the attacks of pitting/corrosion.
- Prevent unnecessary maintenance
- Identification and evaluation of degradation, failures and malfunctions of the canister systems caused by aging effects and CISCC.
- ISFSIF risk level assessment.
- Optimization of ISFSIF operational conditions and practices to reduce aging degradation
- Identification of new emerging aging effects
- Assessment concerning continued operation of ISFSIF, including reviews of license renewal applications.

This report is concerned only with detection of atmospheric marine environments at ISFSIs site using PFAA and NAA of chlorine. The filed data to be collected will link to the experimental laboratory data and to electrochemical process models that can represent the corrosion process at different stages, constituting facilitation of corrosion management.
III. Dry Fuel Canister Model

Spent nuclear fuel from power reactors is unloaded into a water-filled pool immediately adjacent to the reactor to allow its heat and radiation levels to decrease. It is held in these pools for periods ranging from a few years to decades. After cooling, the fuel may be transferred to massive air-cooled dry casks for storage on site or in a centralized facility.

Two basic types of storage systems are in use in the United States: bare-fuel (thick-walled or metal shielded) casks and canister-based systems consisting of a (thin-walled) canister inside a (thick-walled cask or storage module (concrete-shielded). In bare-fuel cask storage systems, used-fuel assemblies are placed directly into a basket that is integrated into the cask itself and then the cask is sealed using two bolted lids. Most bare-fuel systems are for storage only.

In canister-based storage systems, used-fuel assemblies are loaded into baskets integrated into a thin-wall (typically 0.5 – 0.75 inch) stainless steel cylinder, referred to as a canister. The canister is sealed with two welded lids. Most canister-based systems are designed to be dual-purpose canisters (DPC); that is, the canister can be stored or transported if it is placed within a suitable storage or transportation overpack. The dry storage systems loaded today are all of the DPC type. Originally, some of the early designs were multi-purpose canisters (MPC) that were designed for storage, transportation and direct disposal, but DOE was unable to define suitable disposal criteria. Thus, these canisters are limited to storage and transport only while direct disposal of the canisters is still a possibility. Dual-purpose designs bypass the need for fuel to be returned to the reactor used-fuel pool for repackaging into a transport package. For storage the DPCs or MPCs are placed in either a cylindrical overpack system made up of concrete and steel, or a concrete vault-type overpack system. The overpack protects the canister against external man-made events and external natural phenomena, and functions as a shielding/thermal barrier. The overpack is typically closed with a bolted lid. Shown in Figure 2 is a typical canister-based storage system (Holtec International’s HI-STORM storage system).

Figure 2. Typical Canister-Based Storage System.
In dry-cask storage, spent fuel assemblies are typically placed in steel canisters that are surrounded by a heavy shielding shell of reinforced concrete, with the shell containing vents allowing air to flow through to the wall of the canister and cool the fuel. A typical dry cask for PWR fuel contains about 10 tons of spent fuel, roughly one-half of an annual discharge from a 1 GWe reactor. In the United States, casks are typically stored at or close to the reactor site. In order to evaluate the storage characteristics of spent fuel, a typical PWR type spent fuel with its initial enrichment of 4.5 wt% of U-235, discharged burn-up of 48 GWd/tU and 10 years of cooling time was selected as a reference base. Table 1, Table 2, Table 3, and Table 4 provide information on typical dry fuel storage systems for comparison, while delivering the data for the storage system employed in the MCNP6 models used in this paper for the detection of chloride: the VSC-24 storage system. Most dry storage systems have very similar dimensions: cavity height of 170-200 inches; an inner diameter of 60-70 inches; and a cask outer diameter of 90-100 inches if a steel shielding system is implemented, and up to 130 inches if equipped with a concrete overpack shielding system.
Table 1. Characteristics of Dry Cask Storage-Only Systems in the United States- Basic Design Information.

<table>
<thead>
<tr>
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<th></th>
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</thead>
<tbody>
<tr>
<td>CASTOR V/21</td>
<td>CERT-1000 Surry (SNM-2501)</td>
<td>vertical metal cask on concrete pad</td>
<td>Cast Iron, SS, BSS, Ni Coating, Polyethylene, Epoxy Resin Coating, Elastomer Seals</td>
<td>94.5&quot;</td>
<td>bolted</td>
<td>21 PWR</td>
<td>3.6</td>
<td>35</td>
<td>6</td>
<td>21.1</td>
<td>BPRAs</td>
<td></td>
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<tr>
<td>Castor X/325</td>
<td>Under Review (72-1028)</td>
<td>vertical carbon steel cask with borated aluminum (NAM) rods on concrete pad</td>
<td>CS, SS, Al, Polyethylene, Al-B4C Composite, Flame-sprayed Al, Inconel, Viton, BROCOPHAN, Silicon Sealant</td>
<td>91.6&quot;</td>
<td>1) Bolted inner and outer 2) Bolted inner, welded outer</td>
<td>32 PWR</td>
<td>5.0</td>
<td>45</td>
<td>2.9 - 9.5</td>
<td>32</td>
<td>BPRAs</td>
<td></td>
</tr>
<tr>
<td>NAC-S/T</td>
<td>CERT-1002</td>
<td>vertical metal cask on concrete pad</td>
<td>SS, Pb, Al, Cu, NS4FR, Boral</td>
<td>94&quot;</td>
<td>bolted</td>
<td>26 PWR</td>
<td>3.3</td>
<td>35</td>
<td>5</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAC-C28 S/T</td>
<td>CERT-1003</td>
<td>vertical metal cask on concrete pad</td>
<td>SS, Pb, Al, Cu, NS4FR, Boral</td>
<td>94&quot;</td>
<td>bolted</td>
<td>28 PWR</td>
<td>3.5</td>
<td>35</td>
<td>10</td>
<td>20</td>
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<td></td>
</tr>
<tr>
<td>NAC-I28 S/T</td>
<td>Surry approved TSAR (SNM-2501) No Certificate</td>
<td>vertical metal cask on concrete pad</td>
<td>SS, Pb, Al, Cu, NS4FR, Boron Impregnated Al, Silicone Foam</td>
<td>95.2&quot;</td>
<td>bolted</td>
<td>28 PWR</td>
<td>1.9</td>
<td>35</td>
<td>10</td>
<td>15.6</td>
<td>BPRAs, TPDs</td>
<td></td>
</tr>
<tr>
<td>TN-24</td>
<td>CERT-1005</td>
<td>vertical metal cask on concrete pad</td>
<td>CS, Al, Zr/Al &amp; TAVI-Oxide Coatings, Cu, Borated Polyester Resin, Borated SS, SS, Al, Vilon O-rings, Polypropylene</td>
<td>94.8&quot;</td>
<td>bolted</td>
<td>24 PWR</td>
<td>3.5</td>
<td>35</td>
<td>5</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN-32</td>
<td>CERT-1021</td>
<td>vertical metal cask on concrete pad</td>
<td>CS, Al Coating, Al SS, Borated Polyester Resin, Borated Aluminum, Vilon, Polypropylene</td>
<td>97.8&quot;</td>
<td>bolted</td>
<td>32 PWR</td>
<td>4.65</td>
<td>45</td>
<td>7 (&quot;13&quot;)</td>
<td>32.7</td>
<td>BPRAs, TPAs</td>
<td></td>
</tr>
<tr>
<td>TN-32A</td>
<td>CERT-1021</td>
<td>vertical metal cask on concrete pad</td>
<td>CS, Al Coating, Al SS, Borated Polyester Resin, Borated Aluminum, Vilon, Polypropylene</td>
<td>97.8&quot;</td>
<td>bolted</td>
<td>32 PWR</td>
<td>4.65</td>
<td>45</td>
<td>7 (&quot;13&quot;)</td>
<td>32.7</td>
<td>BPRAs, TPAs</td>
<td></td>
</tr>
<tr>
<td>TN-32B</td>
<td>CERT-1021</td>
<td>vertical metal cask on concrete pad</td>
<td>CS, Al Coating, Al SS, Borated Polyester Resin, Borated Aluminum, Vilon, Polypropylene</td>
<td>97.8&quot;</td>
<td>bolted</td>
<td>32 PWR</td>
<td>4.65</td>
<td>45</td>
<td>7 (&quot;13&quot;)</td>
<td>32.7</td>
<td>BPRAs, TPAs</td>
<td></td>
</tr>
<tr>
<td>TN-40</td>
<td>Prarie Is. (SNM-2506)</td>
<td>vertical metal cask on concrete pad</td>
<td>CS, Al, Zn/Al Coating, Borated Polyester Resin, Vilon, Polypropylene, SS, Boral</td>
<td>101&quot;</td>
<td>bolted</td>
<td>40 PWR</td>
<td>3.85</td>
<td>45</td>
<td>10</td>
<td>27</td>
<td>BPRAs, TPDs</td>
<td></td>
</tr>
<tr>
<td>VSC-24</td>
<td>CERT-1007</td>
<td>vertical concrete overpack w/ metal sealed basket &amp; transfer cask</td>
<td>Ceramic Tiles, CS, SS, Concrete, Vilon O-rings, Rn-277, Coatings (*14)</td>
<td>132&quot;</td>
<td>welded casker, bolted overpack</td>
<td>24 PWR</td>
<td>4.2</td>
<td>45</td>
<td>5 (&quot;13&quot;)</td>
<td>24</td>
<td>BPRAs, TPAs</td>
<td></td>
</tr>
<tr>
<td>MC-10</td>
<td>Inel/Surry approved TSAR (SNM-2501) CERT-1001 (NOTE: Letter in for termination of CoC)</td>
<td>vertical metal cask on concrete pad</td>
<td>SS, CS, Low Alloy Steel, Ni33, Al, Bic, Ni, Boral, Inconel, Carto-Zinc8 Coating, Ethylene, Polypropylene, Polyacrylate</td>
<td>94.3&quot;</td>
<td>welded (TSAR says bolted &amp; 3rd cover can be welded)</td>
<td>24 PWR</td>
<td>3.7</td>
<td>35</td>
<td>10</td>
<td>13.5</td>
<td>BPRAs, TPDs</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Characteristics of Dry Cask Storage-Only Systems in the United States- Detailed Dimensions.

| Cask Name | ID (in) | OD (in) | Cavity Height (in) | Outer Height (in) | Wall Thickness (in) | Base Thickness (in) | Structural Lid Thickness (in) | Max Wt (ton) (°8) | Cavity Height (in) | OD (in) (°7) | Height (in) (°7) | Base Thickness (in) | Structural Lid Thickness (in) | Radial N Shield Thickness (in) | Inner Shell Thickness (in) | Gamma Shield Thickness (in) | Total Wall Thickness (in) (°25) | Max Wt (ton) (°8) |
|-----------|---------|---------|--------------------|------------------|-------------------|-------------------|-----------------------|----------------|----------------|-------------|----------------|----------------|-------------------|-----------------|----------------|-----------------|--------------------------|----------------|----------------|
| CASTOR V/21 | N/A     |         |                    |                  |                   |                   |                       |                | 163.5         | 60.1        | 94.5          | 192.4       | 13.8              | 3.5              | (°22)            | N/A             | (°22)            | 11.8           | 117.7            |                     |                |                |                |                          |                |                |
| Castor X/32S | N/A     |         |                    |                  |                   |                   |                       |                | 163.6         | 68.1        | 91.6          | 190.9       | 8.4               | 14.9             | (°22)            | N/A             | (°22)            | 11.8           | 117.7            |                     |                |                |                |                          |                |                |
| NAC-S/T   | N/A     |         |                    |                  |                   |                   |                       |                | 166           | 64.8        | 94            | 183.3(°15) | 8.8               | 8.5              | 7                 | 1.5             | 3.2             | 14.6           | 81.1(empty)      |                     |                |                |                |                          |                |                |
| NAC-C28 S/T | N/A     |         |                    |                  |                   |                   |                       |                | 166           | 64.8        | 94            | 183.3(°15) | 8.8               | 8.5              | 7                 | 1.5             | 3.2             | 14.6           | 83(empty)        |                     |                |                |                |                          |                |                |
| NAC-D28 S/T | N/A     |         |                    |                  |                   |                   |                       |                | 166           | 64.8        | 95.2         | 183.3(°15) | 8.8               | 8.5              | 7                 | 1.5             | 3.2             | 15.2           | 102.9            |                     |                |                |                |                          |                |                |
| TN-24     | N/A     |         |                    |                  |                   |                   |                       |                | 163.3         | 63          | 94.8          | 201         | 11.3              | 11.5             | 5.4               | N/A             | 9.8             | 15.9           | 108              |                     |                |                |                |                          |                |                |
| TN-32     | N/A     |         |                    |                  |                   |                   |                       |                | 163.3         | 68.8        | 97.8          | 202.3       | 10.3              | 4.5              | 4.5               | 1.5             | 8              | 14.5           | 115.5            |                     |                |                |                |                          |                |                |
| TN-32A    | N/A     |         |                    |                  |                   |                   |                       |                | 164.4         | 68.8        | 97.8          | 202.3       | 10.3              | 4.5              | 4.5               | 1.5             | 8              | 14.5           | 115.6            |                     |                |                |                |                          |                |                |
| TN-32B    | N/A     |         |                    |                  |                   |                   |                       |                | 163.3         | 68.8        | 97.8          | 202.3       | 10.3              | 4.5              | 4.5               | 1.5             | 8              | 14.5           | 115.6            |                     |                |                |                |                          |                |                |
| TN-40     | N/A     |         |                    |                  |                   |                   |                       |                | 163           | 72          | 101           | 201.6       | 10.3              | 4.5              | 4.5               | 1.5             | 8              | 14.5           | 115.6            |                     |                |                |                |                          |                |                |
| VSC-24    | 60.5    | 62.5    | 150.6 - 179.6      | 164.2 - 192.2     | 1                 | 0.8              | 3                   | 28.4 - 34.3      | 171.9         | 70.5        | 132           | 196.7 - 225.1 | 2 (°23)         | 0.8              | 29                | 1.8             | 1.8             | 30.8           | 126.4 - 143.9 |                     |                |                |                |                          |                |                |
| MC-10     | N/A     |         |                    |                  |                   |                   |                       |                | 164.1         | 68.3        | 94.3(°15)   | 191.9(TSAR) | 11               | 3.5              | 3                 | 10              | 10             | 13.1           | 119.8(TSAR)      | 113.3(CuC)       |                     |                |                |                |                          |                |                |

Notes:
(°1) - Materials abbreviations
- DU = depleted uranium
- B4C = boron carbide
- KS = carbon steel
- SS = stainless steel
- KB4 = potassium tetraborate
- BSS = boron-stainless steel
- Al = aluminum
- Zn = zinc
- SN = nickel
- Cu = copper
- Pb = lead
- Ti = titanium
- Zr = zirconium
- Al-B = aluminum-boron

(°2) - Primary containment boundary closures.

(°7) - Dimension doesn't include impact limiters.

(°8) - Max wt is with canister/cask fully loaded and excludes impact limiters.

(°15) - Includes additional neutron shield for top that would add another 6° to the height listed in the table.

(°22) - Two concentric rings of poly rods in the cast iron, rod's D = 6" for Castor V/21 and rod's D = 7.25" for Castor X/32S.

(°23) - Base sits 22" above cask bottom.
Table 3. Characteristics of Multi-Purpose Dry-Storage Systems in the United States- Basic Design Information.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Status</th>
<th>Description</th>
<th>Cask System Design</th>
<th>Fuel Characteristics</th>
<th>Unique Contents</th>
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<td>Holtec Hi-STAR 100</td>
<td>Certificate (71-9261)</td>
<td>vertical metal overpack w/ dual-purpose canister &amp; 3 basket assemblies</td>
<td>60 BWR (68F BWR)</td>
<td>24 PWR</td>
<td>Zr/SS clad fuel, fast fuel</td>
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<tr>
<td>(transport)</td>
<td></td>
<td>SS, CS, Al, Holite-A Paints, Boral</td>
<td>24.6-44.1 PWR</td>
<td>30 BWR (68F)</td>
<td>BWIR MOX fuel, Thoria rods, Thoria FAs w/ 3Be neutron source</td>
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<tr>
<td></td>
<td></td>
<td>Aluminum honeycomb in stainless steel skin, bolted overpack</td>
<td>24.6-44.1 PWR</td>
<td>Min. Cool Time (yr)</td>
<td>9.9-16.9 PWR</td>
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<td>vertical metal overpack w/ dual-purpose canister &amp; 3 basket assemblies</td>
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<td>24.6-44.1 PWR</td>
<td>Max. Burnup (GWD/MTU)</td>
<td>7.82 BWR (68F)</td>
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<tr>
<td>TN-68</td>
<td>Certificate (71-9253)</td>
<td>metal cask for transport of BWIR FAS</td>
<td>60 BWR (68F BWR)</td>
<td>24 PWR</td>
<td>Zr/SS clad fuel, fast fuel</td>
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<tr>
<td>(transport)</td>
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<td>CS, AI, AI-B Alloy, Pb, Boraxin, Borated Polymer Resin (NOT N54FR)</td>
<td>30-47 BWR</td>
<td>Min. Cool Time (yr)</td>
<td>BWIR MOX fuel, Thoria rods, Thoria FAs w/ 3Be neutron source</td>
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<td>bolted</td>
<td>30-47 BWR</td>
<td>12.5-18 PWR</td>
<td>PWR control components, BWIR MOX, Thoria rods, PWR &amp; BWIR damaged fuel and fuel debris</td>
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<tr>
<td>TN-68</td>
<td>Certificate (72-1027)</td>
<td>metalic cask on concrete pad</td>
<td>68 BWR</td>
<td>5-15 PWR</td>
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<tr>
<td>(storage)</td>
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<td>CS, AI, SS, Polypropylene, Al-B Alloy, Pb, Boraxin, Borated Polymer Resin</td>
<td>10-12 PWR</td>
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<td></td>
<td></td>
<td>(NOT N54FR)</td>
<td>10-12 PWR</td>
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<td>TN-FSV</td>
<td>Certificate (71-9253)</td>
<td>Steel and lead shielding shipping cask for Fort St. Vrain (FSV) and Peach Bottom (PB1)</td>
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<td>1600 days FSV</td>
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<td>(storage)</td>
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<td>SS, Pb, Silicone/Eutyl O-nings, Al, DU</td>
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<td>1600 days FSV</td>
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Table 4. Characteristics of Multi-Purpose Dry-Storage Systems in the United States - Detailed Dimensions.

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</tbody>
</table>
The composition, heat output and radioactivity per ton of heavy metal of the spent fuel depend upon the burn-up. For PWR spent fuel with a burnup of 50 GWd/THM, the spent fuel consists of about 93.4% uranium (~0.8% U-235), 5.2% fission products, 1.2% plutonium (12 kg or 1.5 weapon equivalents per ton of fuel), and 0.2% minor transuranic elements (neptunium, americium, and curium). As the radioactive elements in the spent fuel decay, they produce heat. As the abundance of these elements decreases with time, so does the heat production. Figure 3 shows the reduction in decay heat for the first 100 years after the fuel has left the reactor for a range of past, current, and likely future burnups for low-enriched uranium LWR fuel.

![Figure 3. Decay heat as a function of time from 0.01 years (about 4 days) to 100 years for low-enriched uranium spent-fuel with burnups of 33, 43, 53 and 63 GWd/THM. The lowest burnup was typical for the 1970s. Current burnups are around 50 GWd/THM. Source: Robert Alvarez, Jan Beyea, Klaus Janberg, Jungmin Kang, Ed Lyman, Allison Macfarlane, Gordon Thompson, and Frank N. von Hippel, "Reducing the Hazards from Stored Spent Power-Reactor Fuel in the United States," Science and Global Security, volume 11, 2003, pp. 1-15.](image)

One technical requirement for the chosen fuel storage system is that all hardware for use with the fuel assemblies are constructed to be compatible with both Westinghouse and B&W 17x17 fuel assemblies (see Table 5 below). The thermal power output of the spent fuel has also been experimentally determined at a value of ~1.724 kW/tHM [1]. Given the heavy metal mass of a 24 unit spent fuel canister to be about 10,560 kg (11.64 tons), this gives a total power output of 20,067 W (0.02 MW) for a typical 24 unit spent fuel storage system. The value of 1.724 kW/tHM corroborates the data above and is the value employed in this analysis for proper scaling of MCNP6 tallies.
Table 5. Physical Characteristics of LWR and PWR Fuel Assemblies [9].

<table>
<thead>
<tr>
<th></th>
<th>BWR</th>
<th>PWR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall assembly length (m)</td>
<td>4.470</td>
<td>4.059</td>
</tr>
<tr>
<td>Cross section (cm)</td>
<td>13.9x13.9</td>
<td>21.4x21.4</td>
</tr>
<tr>
<td>Fuel pin array</td>
<td>8x8</td>
<td>17x17</td>
</tr>
<tr>
<td>Fuel pins/assembly</td>
<td>63</td>
<td>264</td>
</tr>
<tr>
<td>Nominal volume/assembly (m³)</td>
<td>0.0864</td>
<td>0.186</td>
</tr>
<tr>
<td>Assembly total weight (kg)</td>
<td>275.7</td>
<td>657.9</td>
</tr>
<tr>
<td>Uranium/assembly (kg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>183.3</td>
<td>461.4</td>
</tr>
<tr>
<td>Discharge</td>
<td>176.5</td>
<td>441.2</td>
</tr>
<tr>
<td>Enrichment (wt% U³⁹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>2.75</td>
<td>3.20</td>
</tr>
<tr>
<td>Discharge</td>
<td>0.69</td>
<td>0.84</td>
</tr>
<tr>
<td>Plutonium/assembly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at discharge</td>
<td>1.54</td>
<td>4.18</td>
</tr>
<tr>
<td>Other TRU elements/assembly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at discharge</td>
<td>0.10</td>
<td>0.43</td>
</tr>
<tr>
<td>Fission products/assembly</td>
<td></td>
<td></td>
</tr>
<tr>
<td>at discharge</td>
<td>5.2</td>
<td>15.7</td>
</tr>
<tr>
<td>Average discharge burnup</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MW-d/tonne initial uranium)</td>
<td>27,500</td>
<td>33,000</td>
</tr>
<tr>
<td>Average thermal power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(kW/assembly)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge</td>
<td>278</td>
<td>1,017</td>
</tr>
<tr>
<td>1 year after discharge</td>
<td>1.3</td>
<td>4.7</td>
</tr>
<tr>
<td>10 years after discharge</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Average radioactivity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(megacuries/assembly)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge</td>
<td>28.3</td>
<td>102.0</td>
</tr>
<tr>
<td>1 year after discharge</td>
<td>0.35</td>
<td>1.16</td>
</tr>
<tr>
<td>10 years after discharge</td>
<td>0.06</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Los Alamos National Laboratory (LANL) conducted an in-depth analysis of a typical Westinghouse pressurized water reactor [2], providing accurate used fuel isotopic data describing a single unit (17x17 fuel storage assembly), with accurate fuel compositions after 1, 5, 20, 40, and 80 years of cooling time. The study pertains to The Next Generation Safeguards Initiative (NGSI) spent fuel library for 30 GWd and 45 GWd fuel at 5 different cooling times. The NGSI library was created using MONTEBURNS, which is way of combining MCNP and ORIGEN to generate spent fuel nuclide inventories.

The fuel composition from the LANL analysis (a burnup of 45 GWd) was gathered and material cards created for implementation into MCNP6 models to begin obtaining NAA data for a cooling time of 5, 10, 20, 40, and 80 years, with a focus on 10 years presently (see Appendix E for the material card used in the MCNP6 model as gathered from the above analysis). The 10-year data was gathered by taking the median between the 5-year and 20-year values for each isotope of the material cards.

For this report, the MCNP6 model used replicates the Holtec, International and Sierra Nuclear Corporation VSC-24 storage system.

- Helium back-filled
- 17x17 spent fuel storage units (24 count)
- SS304 canister thickness = 5/8"
- Air gap between outer wall of canister and inner wall of concrete overpack = 3"
- A total concrete thickness of 50 cm
- Concrete shelled with surfaces at 10 cm intervals for tally analysis

The MCNP6 model can be viewed below in Figure 4 and Figure 5. The concrete overpack, as seen in Figure 4, was shelled into 10 cm increments in order to tally particle data in stages throughout the shielding system. This design is also very similar in all geometrical aspects to the Sierra Nuclear Corporation’s TranStor Storage System (making up an ISFSI on the site of the Trojan Nuclear Plant in Columbia County, Oregon; to the Holtec International HI-STORM Storage System; as well as to the Westinghouse MC-10 PWR storage system (although the MC-10 employs a steel shielding system rather than a concrete overpack). Table 6 below provides information of the concrete used in this analysis [10] and Table 7 provides the composition of the SS304L modeled to describe the stainless steel canister (Appendix F).

![Figure 4. Cross-Section of the 24 Unit Spent Fuel System Modeled in MCNP6.](image)
Figure 5. Quarterly Cross-Section View of a Typical PWR Fuel Storage System.

Table 6. CONCRETE [LOS ALAMOS (MCNP) Mix] - Density = 2.25 g/cm³

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Weight Fraction</th>
<th>Atom Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.00453</td>
<td>0.006094</td>
</tr>
<tr>
<td>O</td>
<td>0.5126</td>
<td>0.043421</td>
</tr>
<tr>
<td>Si</td>
<td>0.36036</td>
<td>0.01739</td>
</tr>
<tr>
<td>Al</td>
<td>0.03555</td>
<td>0.001786</td>
</tr>
<tr>
<td>Na</td>
<td>0.01527</td>
<td>0.0009</td>
</tr>
<tr>
<td>Ca</td>
<td>0.05791</td>
<td>0.001958</td>
</tr>
<tr>
<td>Fe</td>
<td>0.01378</td>
<td>0.000334</td>
</tr>
</tbody>
</table>
Table 7. Material Composition of Canister - Density = 7.92 g/cm$^3$

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Weight Fraction</th>
<th>Atom Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.705280</td>
<td>0.678055</td>
</tr>
<tr>
<td>C</td>
<td>0.000216</td>
<td>0.000966</td>
</tr>
<tr>
<td>Mn</td>
<td>0.018325</td>
<td>0.017909</td>
</tr>
<tr>
<td>Si</td>
<td>0.002510</td>
<td>0.004798</td>
</tr>
<tr>
<td>Cr</td>
<td>0.183257</td>
<td>0.189225</td>
</tr>
<tr>
<td>Ni</td>
<td>0.081143</td>
<td>0.074226</td>
</tr>
<tr>
<td>P</td>
<td>0.000325</td>
<td>0.000563</td>
</tr>
<tr>
<td>S</td>
<td>0.000010</td>
<td>0.000017</td>
</tr>
<tr>
<td>N</td>
<td>0.008933</td>
<td>0.034241</td>
</tr>
</tbody>
</table>

III. A. Atmospheric Marine Data

The typical composition of seawater by dry weight percent includes: 55.5% chloride; 30.8% sodium; 7.7% sulfate; 3.7% magnesium; 1.2% calcium; 1.1% potassium. The chemical composition of the Great Salt Lake is similar to that of typical ocean water. Sodium and chloride are the major ions in the water, followed by sulfate, magnesium, calcium, and potassium. For comparison, the table below (Table 8) shows the concentration of the six major ions in water of the Great Salt Lake, a typical ocean, and the Dead Sea [3].

Table 8. Composition of Sea-Salt

<p>| Chemical Composition (Dry Weight Percent) of Great Salt Lake, Typical Ocean, and The Dead Sea Waters. |
|---------------------------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Source</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Magnesium</th>
<th>Calcium</th>
<th>Chloride</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Great Salt Lake</td>
<td>32.8</td>
<td>2</td>
<td>3.3</td>
<td>0.2</td>
<td>54.5</td>
<td>7.2</td>
</tr>
<tr>
<td>Ocean (typical)</td>
<td>30.8</td>
<td>1.1</td>
<td>3.7</td>
<td>1.2</td>
<td>55.5</td>
<td>7.7</td>
</tr>
<tr>
<td>Dead Sea</td>
<td>12.3</td>
<td>2.3</td>
<td>12.8</td>
<td>5.3</td>
<td>67.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The typical ocean salt from the above table was used in this chloride detection analysis.
IV. Chloride Deposition Analysis

The amount of Chloride deposited on the SS304L outer canister surface was gathered from the information found on pages 8 and 29 of the proposal report. In the report the lower range of salt deposition observed and reported is between 300 mg/m$^2$ and 5 mg/m$^2$. This is the lower limit (with the addition of 1000 mg/m$^2$) implemented into the MCNP6 model to obtain photon flux data for determining the threshold detection limit of chloride, as well as for constructing a curve describing gamma counts vs. chloride amount for various energies that are signatures for the presence of chloride.

Table 9 and Table 10 provide the air and sea salt elemental information used in this analysis to evaluate the feasibility of detecting chloride overlaying the outside surface of a stainless steel canister. With an outer SS304L canister surface area of 24.61 m$^2$, the data was obtained for various sea salt deposition amounts, of which is provided in Table 11 below. An Air/Sea-Salt film (t = .25 mm) covering the outer surface of the SS304L canister was employed in my model. The density of dry air used was .0012 g/cm$^3$; the density of chloride is 2.03 g/cm$^3$; the density of sea salt is 2.165 g/cm$^3$.

<table>
<thead>
<tr>
<th>Table 9. Dry Air Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Air Composition</td>
</tr>
<tr>
<td>Element</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>Ar</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 10. Sea Salt Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea Salt Composition</td>
</tr>
<tr>
<td>Element</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>Amount of Chloride Coating Surface of SS316L Canister (mg/m²)</td>
</tr>
<tr>
<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>Film Volume (cm³)</td>
</tr>
<tr>
<td>Dry Air Volume (cm³)</td>
</tr>
<tr>
<td>Sea Salt Volume (cm³)</td>
</tr>
<tr>
<td>Mass of Air (g)</td>
</tr>
<tr>
<td>Mass of Sea Salt (g)</td>
</tr>
<tr>
<td>Air Wt%</td>
</tr>
<tr>
<td>Sea Salt Wt%</td>
</tr>
<tr>
<td>Total Density of Air/Sea-Salt Mixture (g/cm³)</td>
</tr>
<tr>
<td>Atomic Density of Mixture (atoms/b-cm)</td>
</tr>
</tbody>
</table>

**IV.A. Gamma Emission from Neutron Induced Reactions**

Neutron activation provides elemental material composition. Density and mass can be identified if sufficient counts are collected by a gamma detector, with the probability of identification increasing with time.

Gamma rays, which are emitted from radioactive nuclei that form after neutron bombardment, provide a unique gamma-energy spectral signature for each element. Techniques that measure transmitted, attenuated, or scattered neutrons can provide imaging, as well as information about elemental composition. Being electrically neutral, neutrons do not interact strongly with matter.

Neutrons bombard the nuclei of unknown materials. The neutrons are scattered or absorbed by the nuclei, emitting gammas of specific energies, depending on the neutron initial energy and the specific nucleus. Analysis of the emitted gammas can provide material composition and density of the unknown material.

**IV.B. Gamma Flux Analysis**

Natural chlorine consists of two isotopes, $^{35}\text{Cl}$ (75.5%) and $^{37}\text{Cl}$ (24.5%). There are two types of thermal and epithermal neutron reactions with chlorine, that produce unique gamma-ray signatures; the first and more dominant reaction is $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$, where $^{36}\text{Cl}$ is a radioactive isotope (half-life of $3.0\times10^5$ years) that upon decay, emits gamma ray energies of 517, 786, 1165, 1951 keV and 6.1 and 7.4 MeV. See Appendix A for the decay scheme of $^{36}\text{Cl}$ [4][5]. The second is $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$; $^{38}\text{Cl}$ is an unstable isotope with a half-life of 37.3 minutes, that decays by emission of a $\beta$ particle and a $\gamma$ ray with an energy of 1.64 or 2.17 MeV, and forms a stable argon isotope, $^{38}\text{Ar}$. See Appendix B for the decay scheme of $^{38}\text{Cl}$ [6]. The neutron activation analysis (NAA) sensitivity is dependent on neutron flux, irradiation time, and
sample mass, detector counting efficiency, background, and counting time. The thermal cross section of $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ is 43 barn (epithermal is 18 barns), as compared to 0.4 barns for $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$.

After the tally data from the MCNP6 simulations are gathered, the values must be scaled appropriately in order for the gamma flux to be estimated accurately. The following equation is employed to determine the photon flux for a particular gamma signal:

$$\phi\left[\frac{\gamma}{cm^2 \cdot s}\right] = \frac{F_2 \cdot p}{1.6022 \times 10^{-19}} \cdot \frac{\text{photons}}{[\text{fission neutron}]} \cdot \frac{[\text{MW}]}{[\text{fission}]} \cdot \frac{n}{[\text{fission}]} \cdot \text{Tally Weighting Factor}$$

The ‘Tally Weighting Factor’ is the percentage of the interested energy bin tally to the total tally. Table 12 provides the concomitant fuel storage system values necessary to evaluate the detection of chloride of a spent fuel storage system. As stated earlier in this report, the power output of a typical spent fuel canister for which the MNCP6 tallies were scaled to has the value of 20,000 W (or 0.02 MW).

<table>
<thead>
<tr>
<th>Table 12. MCNP6 Supporting Data for Photon Flux Calculations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCNP6 results for a SNC VSC-24 Storage System</td>
</tr>
<tr>
<td>Criticality Eigenvalue</td>
</tr>
<tr>
<td>Q Value (MeV/fission)</td>
</tr>
<tr>
<td>$\nu$ (neutrons/fission)</td>
</tr>
</tbody>
</table>

After incorporating the data above within the photon flux equation, we are equipped with the following:

$$\phi\left[\frac{\gamma}{cm^2 \cdot s}\right] = \frac{X}{1.6022 \times 10^{-19}} \cdot \frac{\text{photons}}{[\text{fission neutron}]} \cdot \frac{[\text{MW}]}{[\text{fission}]} \cdot \frac{n}{[\text{fission}]} \cdot 0.02 \cdot 2.702 \cdot 198 \cdot 0.377 \cdot \text{TWF}$$

The data below incorporates the sea salt constituents for each associated chlorine amount. The MCNP6 simulations were performed with a source particle count of $5.0 \times 10^9$, with an associated error of $\leq 0.04$. The 6.1 MeV gamma peak and the 7.41 MeV gamma peak, associated with the $^{35}\text{Cl}(n,\gamma)^{36}\text{Cl}$ reaction, were easily captured visually by scanning the MCNP6 tally reaction curves (each curve with a differing amount of sea-salt, the one associated with a chlorine amount of 1000 mg/m² primarily inspected for recognizable peaks that could then be more closely scrutinized for lesser amounts of chloride), which were gathered by tallying 500 energy intervals within short ranges corresponding to each peak. Figure 6 provides the background data (no chloride present) while Figure 7 provides the 7.41 MeV signal (implementing a chlorine amount of 300 mg/m²) as a function of concrete thickness, markedly present and distinguished from the background signal.

Figure 8 provides the curve, at the outside of the concrete overpack, describing the 7.41 MeV signal associated with the decay of Cl-36. Figure 9 provides the curve, at the outside of the concrete overpack, describing the 6.11 MeV signal associated with the decay of Cl-36. A neutronic simulation was also conducted that tallied the outside surface of the concrete overpack in 10000 energy intervals within the range of 0.5 MeV to 7.5 MeV to very accurately discern the interested peaks from the background: regarding the 6.11 MeV chloride peak, it was only discernible from the latter tally due to the proximity of
a much stronger 6.10 MeV background signal and a slightly lighter 6.13 MeV background signal; this signal may hinder our abilities to separate the 6.11 MeV chloride peak from the background noise. The data for each of these two peaks are given in Table 13 and Table 14, for the 6.11 MeV photon and the 7.41 MeV photon, respectively. The data at 50 cm is taken to be outside of the concrete overpack, where a detector could be located.
Figure 6. Background Signal – No Chloride Present
Figure 7. 7.41 MeV Gamma Signal from the Decay of Cl-36.
Figure 8. 7.41 MeV Signal from Cl-36, as a Function of Chlorine Amount, Alongside Background Signal at Outside Surface of Concrete Overpack.
6.11 MeV Cl-36 Signal Alongside the Background Signal at Outside Surface of Concrete Overpack

![Graph showing 6.11 MeV signal from Cl-36, as a function of chlorine amount, alongside background signal at outside surface of concrete overpack.]

Figure 9. 6.11 MeV Signal from Cl-36, as a Function of Chlorine Amount, Alongside Background Signal at Outside Surface of Concrete Overpack.

<table>
<thead>
<tr>
<th>Distance through Concrete (cm)</th>
<th>1000 mg/m² Cl (m²/cm²·s)</th>
<th>300 mg/m² Cl (m²/cm²·s)</th>
<th>150 mg/m² Cl (m²/cm²·s)</th>
<th>75 mg/m² Cl (m²/cm²·s)</th>
<th>30 mg/m² Cl (m²/cm²·s)</th>
<th>5 mg/m² Cl (m²/cm²·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>120</td>
<td>91</td>
<td>68</td>
<td>46</td>
<td>23</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 13. Results for the 6.11 MeV Photon.
<table>
<thead>
<tr>
<th>Distance through Concrete (cm)</th>
<th>1000 mg/m² Cl ( \frac{\gamma}{cm^2 \cdot s} )</th>
<th>300 mg/m² Cl ( \frac{\gamma}{cm^2 \cdot s} )</th>
<th>150 mg/m² Cl ( \frac{\gamma}{cm^2 \cdot s} )</th>
<th>75 mg/m² Cl ( \frac{\gamma}{cm^2 \cdot s} )</th>
<th>30 mg/m² Cl ( \frac{\gamma}{cm^2 \cdot s} )</th>
<th>5 mg/m² Cl ( \frac{\gamma}{cm^2 \cdot s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>42775</td>
<td>25193</td>
<td>14190</td>
<td>6332</td>
<td>1597</td>
<td>63</td>
</tr>
<tr>
<td>10</td>
<td>2186</td>
<td>1279</td>
<td>716</td>
<td>320</td>
<td>81</td>
<td>3.40</td>
</tr>
<tr>
<td>20</td>
<td>337</td>
<td>197</td>
<td>110</td>
<td>49</td>
<td>13</td>
<td>0.59</td>
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<tr>
<td>30</td>
<td>79</td>
<td>46</td>
<td>26</td>
<td>12</td>
<td>3.02</td>
<td>0.16</td>
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<td>40</td>
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<td>15</td>
<td>8.54</td>
<td>3.90</td>
<td>1.03</td>
<td>0.06</td>
</tr>
<tr>
<td>50</td>
<td>18</td>
<td>11</td>
<td>6.01</td>
<td>2.76</td>
<td>0.75</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure 10 and

6.11 MeV Gamma Counts vs Chloride Content
Figure 11 elaborate upon the photon flux data at the outside surface of the concrete overpack with a curve format; error bars are incorporated using $\sigma = \sqrt{N_i}$, where $N_i$ is the number of counts relating to each calculation.
Figure 10. 6.11 MeV Gamma Counts vs. Amount of Chloride.
IV.C. Pulse Height Tally

In MCNP6, a special pulse height tally, the f8 tally, allows for the determination of the true response of a detector with 100% efficiency (without the use of the GEB function), and a more realistic response with the use of a calibration technique implemented into the f8 tally as the GEB function.

In order to have a model that truly represents the interaction between the detectors and the particles measured, the pulse-height simulation in MCNP6 needs a more realistic Gaussian energy distribution. MCNP6 contains a special tally option in which generated parameters from experimental data can be input to the simulation in order to give the spectra the required Gaussian shape. The special tally within MCNP6 is the GEB option. The GEB tally option gives the detector-simulated data a Gaussian shape by using the un-broadened energy input with the calculated spectral data and user-specified tally inputs to solve Eq. (2) (Ref. [8]):

\[ f(E) = Ce^{-\left(\frac{E-E_o}{\Delta A}\right)^2}, \]  

(2)

where \( E \) is the broadened energy, \( E_o \) is the un-broadened energy of the tally, \( C \) is the normalization constant, and \( A \) is the Gaussian width, defined by

\[ A = \frac{FWHM}{2\sqrt{\ln 2}}, \]  

(3)

Figure 11. 7.41 MeV Gamma Counts vs. Amount of Chloride.
In order to obtain the Gaussian width needed to solve Eq. (1), the full-width at half-maximum (FWHM) of real experimental data is indirectly provided by the user by specifying the three parameters (a, b, and c) in Eq. (4) required by the GEB function within the f8 tally:

\[ FWHM = a + b\sqrt{E} + cE^2. \]  

Equation (4)

Appendix D provides the response of a NaI detector with 100% efficiency.

In field experimental data with the use of a detector type on the outside of a storage system would allow for the calibration of the GEB function within the f8 tally in MCNP6. This calibration would allow for accurate future analyses of all storage systems regarding the detection of chloride.
V. Probability of Detection

It is important to get confidence in the capability of detecting the chloride concentration deposited on the surface of the canisters. The detection capability is quantitatively expressed as a probability of detection (POD). The intuitive way to get confidence that the inspection objectives can be met in practice would simply involve demonstrating that the inspection system can indeed find the threshold of chloride concentration under controlled experimental conditions closely simulating the real environment that canister is exposing at different site. In this report section the description of statistical methods and tools that can be used to determine POD.

The numerical data for POD is typically in one of following two forms:

- “Cl concentration data” = measured response of the detectors to a quantity of chloride
- hit/miss data = binary response whether a chloride has been detected or not.

The MIL handbook (MIL-HDBK-1823, 2007) describes approaches to estimate the reliability of NDE systems, provided availability from the experimental data. According to MIL handbook, a 90/95 has become a de facto design criterion. This means for example that the quantity of chloride will be detected with 90% probability with the confidence that in case the experiment is repeated only 5% might fall below threshold of detector detection. The number of amounts of chloride needed for statistical analyses depends naturally on the confidence level required.

Several different functional forms have been presented in the literature for applicability to available POD data. Some of these functions will be tested and applied to specific detectors that will be used to detect chloride. A software for calculating the POD from hit-miss data is described in the MIL handbook and is, in principle, downloadable form the internet. The software, called mh1823 POD, is based on R, which is a statistical and graphics engine freely downloadable. To choose an appropriate function, the software can produce diagnostic curves, two for each link function. A detailed description of the modelling principles and the use of the software is given in (MIL-HDBK-1823 2007).

An example of a logistic function with threshold that can used for POD for various detectors is given below:

\[
\text{POD}(h) = \begin{cases} \\
1 - \frac{1 + \exp(-qh^*)}{1 + \exp(q(h - s - h^*))}, & \text{if } h > s \\
0, & \text{otherwise}
\end{cases}
\]

Where \(S\) is the threshold of detection, Hence, \(h^*\) can be considered as a location parameter indicating the starting point of “good” detection. The first figure displays the POD curves with different values of \(h^*\) where \(s=0.05\) and \(q=20\). It is shown that when \(h = h^*\), the POD at three cases are all about 0.2. The second Figure displays the POD curves with different values of \(q\) where \(s=0.05\) and \(h^*=0.2\). Clearly, \(q\) is an index measuring the quality of detection. Bigger \(q\) implies better detectability.
II. Magnesium and Sodium Deposition Analysis

Magnesium and sodium are constituents of sea-salt with weight percent ratios provided above in Table 10. Table 15 below provides the relevant reaction decay scheme data for the elements magnesium and sodium. The gamma-ray spectra for sodium and magnesium are provided in Appendix C [6]. The detection of gamma signals associated with these two elements has been unsuccessful; magnesium is a very small constituent of sea-salt while sodium is found in concrete (which is the overpack material).

<table>
<thead>
<tr>
<th>Method of Production: $^{26}$Mg(n, $\gamma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_\gamma$ (keV)</td>
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<tr>
<td>170.686</td>
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<tr>
<td>843.76</td>
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<tr>
<td>1014.44</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Method of Production: $^{23}$Na(n,$\gamma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_\gamma$ (keV)</td>
</tr>
<tr>
<td>996.82</td>
</tr>
<tr>
<td>1368.63</td>
</tr>
<tr>
<td>2754.03</td>
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<td>2869.50</td>
</tr>
<tr>
<td>3866.19</td>
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<tr>
<td>4237.96</td>
</tr>
</tbody>
</table>

The following signals, though very faint, have been detected from the MCNP6 simulations and dissociated from the background, but have not yet been investigated: 5.52 MeV; 5.71 MeV; 6.62 MeV; 6.63 MeV; 6.98 MeV. These may be associated with the other elements composing sea-salt: Calcium, Potassium, and Sulfur.
VI. **Neutron Spectrum of Depleted Fuel Storage System**

The neutron spectrum at the outside of the concrete overpack was gathered by employing MCNP6. The neutrons were tallied from 0.0 MeV to 7.5 MeV in 12,000 energy bins with a particle source count of $5 \times 10^5$, with all errors $\leq 0.04$. The neutron spectrum can be found in Figure 12, with a log plot along the y-axis.

![Neutron Spectra of Spent Fuel Canister at Center of Storage System and Outside of Concrete Overpack](image)

*Figure 12. Background Neutron Spectrum of Spent Fuel System.*

Table 16 below provides the neutron proportions, energetically, at the center of the storage system and at the outside of the concrete overpack.

**Table 16. Percentage of Neutrons in the Fast, Intermediate, and Thermal regions.**

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Neutrons at Center of Storage System (%)</th>
<th>Neutrons at Outside of Overpack (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast (0 to 0.625E-06)</td>
<td>0.13</td>
<td>0.80</td>
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<tr>
<td>Intermediate (0.625E-06 to 0.1)</td>
<td>0.58</td>
<td>0.15</td>
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<tr>
<td>Thermal (0.1 to 20)</td>
<td>0.30</td>
<td>0.05</td>
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</table>
VII. Conclusions

If chloride is present in even very small amounts on the outside of the stainless-steel canister of a spent fuel storage system, it has been shown in this report that an estimated small amount can be inferred from the gammas associated with neutron activation analysis of chloride isotopes. From the data presented in this paper it seems very reasonable to focus attention on the 6.11 MeV gamma and the 7.41 MeV gamma (associated with the $^{35}$Cl(n,γ)$^{36}$Cl reaction) in using a high energy detector system to experimentally confirm the presence of chloride on the outside canister of a spent fuel storage system.

The chloride data provided herein will ultimately be correlated with the data from other members of the team as more science is gathered from the various disciplines across this project. The chloride detection data provided within this report will support and associate among numerous factors, including humidity, temperature, location.

More research could be conducted regarding detector type and whether the necessity for an array of detectors employed to map the surface of the concrete overpack should be realized, or whether perhaps a dosimeter should be used for the high-energy gamma detection device. Experimental field data would corroborate the data proposed in this report while allowing for the calibration of such a detector method in MCNP6 for future storage system analyses.
VIII. REFERENCES


### Appendix G  Chlorine-36 Decay Scheme

![Chlorine-36 Decay Scheme Diagram]

<table>
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<tr>
<th>Isotope</th>
<th>Reaction</th>
<th>$E_{\gamma}$, keV</th>
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<tr>
<td>$^1$H</td>
<td>$(n,\gamma)$</td>
<td>2223</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>$(n,n'\gamma)$</td>
<td>4438</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>$(n,n'\gamma)$</td>
<td>730, 1634, 2313</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>$(n,\gamma)$</td>
<td>1885, 5269, 5298, 10829, 10318</td>
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<td>$^{16}$O</td>
<td>$(n,n'\gamma)$</td>
<td>5618, 6129</td>
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<td>$^{19}$F</td>
<td>$(n,n'\gamma)$</td>
<td>197, 1236, 1348, 1357</td>
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<td>$(n,\gamma)$</td>
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<td>$(n,n'\gamma)$</td>
<td>1266, 2028, 2233</td>
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<td>$(n,n'\gamma)$</td>
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<td>$^{35}$Cl</td>
<td>$(n,\gamma)$</td>
<td>1273, 2230</td>
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<tr>
<td>$^{35}$Cl</td>
<td>$(n,n'\gamma)$</td>
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<td>$(n,\gamma)$</td>
<td>165, 472, 1534, 6810</td>
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</table>

Table 5. Characteristic gamma rays
IV. Appendix B
Chlorine-38 Decay Scheme
**38Cl (37 min.) Decay Scheme**

37 min.

\[ Q = 4916.9 \]

**GAMMA-RAY ENERGIES AND INTENSITIES**

<table>
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<tr>
<th>Nuclide</th>
<th>Half Life: 37.24(5) min.</th>
<th>Detector: 65 cm³ coaxial Ge (Li)</th>
<th>Method of Production: ( ^{38} \text{Cl} ) (n,γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{38} \text{Cl} )</td>
<td></td>
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</tr>
</tbody>
</table>

| \( E_\gamma \) (keV) | \( \sigma_\gamma \) | \( I_\gamma \) (rd) | \( L_\gamma \) (%) | \( \alpha \) | |
|----------------------|------------------|--------------------|-------------------|--------|
| 1642.714             | 78               | 31.9               | 1.0               | 1      |
| 2187.405             | 100              | 42.4               | 1.1               | 1      |

\( E_\gamma \), \( \sigma_\gamma \), \( I_\gamma \), \( \alpha \gamma \) - 1998 ENSDF Data
V. Appendix C

The chlorine material cards were adjusted to incorporate all elements composing sea salt. The gamma peaks for Na and Mg are captured below from an INL gamma-ray spectrum catalogue [6].
$^{27}\text{Mg}(9.4 \text{ min.})$ Decay Scheme

$Q = 2610.32$

$^{27}\text{Mg}$

$^{27}\text{Al}$ stable

GAMMA-RAY ENERGIES AND INTENSITIES

<table>
<thead>
<tr>
<th>$E_\gamma$ (keV)</th>
<th>$\alpha E_\gamma$</th>
<th>$I_\gamma$ (meV)</th>
<th>$I_\gamma$ (%)</th>
<th>$\alpha I_\gamma$</th>
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<td>170.089</td>
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$E_\gamma$, $\alpha E_\gamma$, $I_\gamma$, $\alpha I_\gamma$ - 1998 NSIF Data
\( ^{22}\text{Na}(2.6\text{ yr.}) \text{ Decay Scheme} \)

\[ Q = 2841.2 \]

\[ ^{22}_{11}\text{Na} \]

\[ ^{22}_{10}\text{Ne} \]

\[ ^{2+} \]

\[ 1274.57 \text{ keV} \]

\[ 99.94\% \]

\[ ^{0+} \]

\[ 0 \]

\[ 0.056\% \]

**GAMMA-RAY ENERGIES AND INTENSITIES**

**Nuclide:** \( ^{22}\text{Na} \)

**Half Life:** 2.6019(4) yr.

**Method of Production:** Ne(\(^{4}\text{He},p)\)

<table>
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<tr>
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<th>( \alpha )</th>
<th>( I_\gamma ) (m\text{s})</th>
<th>( I_\gamma ) (%)</th>
<th>( \sigma )</th>
<th>( S )</th>
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<td>0.014</td>
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\( E_\gamma, \sigma, I_\gamma, \sigma_f \) - 1996 ENDF Data
**24Na(14.9 hr.) Decay Scheme**

**GAMMA-RAY ENERGIES AND INTENSITIES**

<table>
<thead>
<tr>
<th>$E_i$ (keV)</th>
<th>$\alpha E_i$</th>
<th>$l_y$ ($\mu$)</th>
<th>$l_i$ (%)</th>
<th>$\alpha l_i$</th>
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$E_i$, $l_y$, $l_i$ - 1998 ENDF Data
$^{25}$Na(59 sec.) Decay Scheme

$^5_0$ Na

Q=3835.3

$^{25}_{12}$ Mg

stable

<table>
<thead>
<tr>
<th>$E_{y}$ (MeV)</th>
<th>$\sigma E_{y}$</th>
<th>$I_{y}$ (pe)</th>
<th>$I_{y}$ (%)</th>
<th>$\alpha I_{y}$</th>
<th>S</th>
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</table>

$E_y$, $\sigma E_y$, $I_y$, $\alpha I_y$ ~ 1998 ENDF Data
VI. Appendix D

Pulse-height tally response for an ideal detector:
VII. Appendix E

Spent fuel material card used in the MCNP6 model:

c 45GWd/MTU: 10 yrs of decay: rho=-10.44174
m25

<p>| | |</p>
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VIII. Appendix F

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NAS hereby certifies that the analysis on this certification is correct. Based upon the results and the accuracy of the test methods used, the material meets the specifications stated. These results relate only to the items tested and this report cannot be reproduced, except in its entirety, without the written approval of NAS.

Technical Dept. Mgr. 

Kris Lapp 

1/15/2016
Chapter 7
Project Summary

BYU was asked to assist LANL in performing nondestructive evaluation (NDE) experiments using two nonlinear acoustic techniques to characterize the size of stress corrosion cracking (SCC) in 304L stainless steel. BYU created rod samples with welds in them and then induced SCC by exposing the samples to hot MgCl$_2$ for different lengths of time to induce different amounts of SCC in the samples. Then BYU researchers applied Nonlinear Resonant Ultrasound Spectroscopy (NRUS) and the Time Reversed Elastic Nonlinearity Diagnostic (TREND) to these samples. The goal of these acoustic experiments was primarily to determine whether the nonlinear acoustic signatures obtained increased with increasing damage. The data show that indeed the nonlinear signatures from NRUS and TREND increase for samples that should have more SCC in them. Three journal manuscripts have been written about this work and they are included to provide the details of BYU’s findings. The first two manuscripts have been published in the journal NDT&E International (comprising pages 3-7 on NRUS experiments to image SCC) and in the Journal of the Acoustical Society of America (comprising pages 8-17 on...
TREND experiments to image SCC. The last manuscript (comprising pages 18-54 on improving TREND techniques applied to SCC imaging) has been submitted and is under review for the Journal of the Acoustical Society of America. Future work after this IRP may include the use of a better TREND technique to image the SCC. This technique was developed in the final year of the project and there was not enough time left to fully explore its implementation. Additionally, the samples created at BYU with the SCC in them may be imaged to determine the actual size of the SCC in them and then this sizing information can then be compared to the nonlinear signatures obtained from NRUS and TREND. Hopefully the nonlinear signatures can then be used to provide an indication of the size and quantity of the SCC present in a sample. For implementation of these nonlinear acoustic techniques on an actual cask, the NRUS and TREND experiments would have to be calibrated for SCC that may be present in the cask. This means that based on the results presented here we expect the nonlinear acoustic signature to increase with larger individual cracks and a higher quantity of cracks in the casks. However, the correlation of an absolute number from a nonlinear acoustics experiment to the crack size and/or the quantity of cracking in a cask needs to still be determined by using these acoustic techniques on a cask with known sizes of SCC. If it is simply desired to know whether the SCC is increasing over time then NRUS and TREND are ready to provide this monitoring capability. If the goal is to predict when an individual crack will penetrate through the cask wall then these techniques will need to be calibrated as stated above.
Nonlinear resonant ultrasound spectroscopy of stress corrosion cracking in stainless steel rods

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Nonlinear resonant ultrasound spectroscopy
Nondestructive evaluation
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\textbf{ABSTRACT}

Stainless steel containers are susceptible to stress corrosion cracking (SCC) under certain stress and corrosion conditions. Nonlinear ultrasonic techniques are very sensitive to the early presence of damage, more so than linear techniques. Nonlinear Resonant Ultrasound Spectroscopy (NRUS) is used here to measure a nonlinear shift in the resonance frequency due to a cumulative amount of SCC. Steel rods are immersed in a heated magnesium chloride solution and removed after different exposure times. NRUS measurements are conducted using the fundamental longitudinal mode of vibration. Rods exposed longer generally have a larger resonance frequency shift and are therefore more nonlinear. Thus NRUS might offer a means of detecting a cumulative SCC damage in a sample.

1. Introduction

Nondestructive evaluation (NDE) methods are needed to characterize damage on 304L stainless steel nuclear storage casks to prevent leakage of radioactivity from cracks [1]. One type of damage of interest is Stress Corrosion Cracking (SCC). SCC occurs when a stress exists, including residual stresses from welding, and the metal is in a corrosive environment (including airborne chlorides) [1]. These conditions result in an electrochemical reaction that makes the metal susceptible to cracking [1]. SCC is most likely to occur in the Heat Affected Zone (HAZ). HAZs are regions of residual stresses created during the welding process. The intense heat of the welding process causes the material properties and grain boundaries within the HAZ to be changed [2]. This affects the strength of the metal and degrades the metal's capacity to resist corrosion, meaning SCC is more likely. SCC can be small enough that visual techniques and linear NDE techniques cannot detect it very easily. Linear NDE techniques often rely on a reflection of sound off of damage (e.g. cracks and delaminations), but if the crack is too small or is a closed crack with the crack surfaces in contact, then no reflection will occur and the crack will be transparent to the incident wave. NDE techniques based on nonlinear acoustics, on the other hand, are well suited to detect closed cracks because surfaces in contact with one another vibrate nonlinearly when excited with sufficiently high amplitude [3]. The full extent of the crack can therefore be measured with nonlinear NDE techniques. Linear techniques also sometimes monitor the ultrasonic attenuation as increases in attenuation are known to be a sign of damage in a sample. As will be discussed in this paper, nonlinear ultrasonics are more sensitive to the presence of damage than the measured changes in attenuation (or quality factor).

Young's modulus is strain independent in linear elasticity, but in damaged materials it depends on the strain experienced by the material. If we strike a damaged steel rod with a hammer harder and harder, a progressively lower frequency tone will be emitted due to nonlinear effects and the apparent material softening (i.e., drop of the elastic constants) [4]. Higher longitudinal strains lower the Young's modulus according to Remillieux et al. [5],

\begin{equation}
E(x) = E_0[1 - \alpha_E \varepsilon_{\text{max}}(x)],
\end{equation}

where \(E(x)\) is amplitude dependent Young's Modulus, \(E_0\) is the undamaged Young's modulus of the bulk material, and \(\varepsilon_{\text{max}}\) is the maximum strain measured in the longitudinal direction during a longitudinal mode of vibration. Here \(\alpha_E\) is a nonclassical nonlinear elastic parameter that has been correlated with inhomogeneity. For instance, freshly milled stainless steel will have a very low, close to zero, \(\alpha_E\). A sedimentary rock, such as sandstone, will have a much larger \(\alpha_E\). Damaged materials will also exhibit a finite value for \(\alpha_E\). Remillieux et al. obtained \(\alpha_E\) from the amplitude dependence of the resonance frequencies of longitudinal modes and then showed that \(\alpha_E\) is different when it is obtained from amplitude dependent shifts of torsional mode resonance frequencies. Prior to the work of Remillieux et al. researchers

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NRUS measures the amplitude dependence of a particular sample's resonance frequency. A swept sine wave excitation signal is used to extract the resonance frequency. The amplitude of the excitation signal is then increased several times and the resulting resonance frequency noted each time. A downward shift in the resonance frequency with increasing strain amplitude is often encountered for damaged materials as the elastic moduli soften (as implied in Eq. (1)). The peak strain at the resonance frequency peak is also extracted. The slope of a plot of the relative frequency shift as a function of strain determines $\alpha_E$ for the sample [6].

NRUS was initially developed to characterize the inherent nonlinearity of natural rock samples such as sandstone, soapstone, and granite [7]. It has been applied to characterize damage in inherently linear materials that normally exhibit no frequency shift in their undamaged state, but that do exhibit a frequency shift in their damaged state, such as fatigue damage in copper and creep damage in stainless steel [8,9]. It has been applied to characterize thermal damage in concrete and damage in bone because even though these materials exhibit a frequency shift in their undamaged state, the shift increases further due to the presence of damage [10–12].

Various nonlinear acoustic techniques have been used to detect and characterize SCC. Ohara et al. developed the Subharmonic Phased Array to image SCC using surface acoustic waves [13,14]. Dynamic Acousto-Elastic Testing employs a low frequency pump and higher frequency probe technique that was used by Rivière et al. to extract $\alpha_E$ and additional nonlinear parameters [15]. Ohara et al. used NRUS to partially locate SCC by analyzing the measured $\alpha_E$ from different resonance modes based on whether the mode had a strain node or antinode at the location of the SCC [16]. An experiment by Morlock et al. used nonlinear Rayleigh surface waves to characterize SCC on four samples with different amounts of SCC [17]. Morlock et al. applied different amounts of stress to two sets of samples while they were exposed to sodium thiosulfate. Within these sets of samples, some were exposed for 1 week while the others were exposed for 3 weeks. They reported an increase in the second harmonic amplitude for the samples will higher stress and with longer exposure time, though they found that the second harmonic amplitude initially decreased with the first week of exposure (relative to a sensitized state) and then returned to its original value after 3 weeks of exposure. Anderson et al. used the Time Reversed Elastic Nonlinearity Diagnostic to explore the depth dependence of SCC near welds [18]. The majority of the nonlinear acoustic techniques were applied to a single sample for proof of concept of the technique's ability to detect SCC rather than being applied to a set of samples with progressive damage. A book reviewing nonlinear ultrasonic techniques was very recently published, which includes a description of the Subharmonic Phased Array, Dynamic Acousto-Elastic Testing, NRUS, Rayleigh waves, and the Time Reversed Elastic Nonlinearity Diagnostic [19].

The purpose of this paper is to determine whether the measured $\alpha_E$ using NRUS correlates with exposure time (likely corresponding to an overall increase in SCC damage) in 304L stainless steel rod samples, and if so, what that functional dependence is. Samples are placed in a hot magnesium chloride (MgCl$_2$) bath for varying lengths of time to induce SCC. Here we excite only the fundamental longitudinal mode of rod samples because that is the type of resonance mostly commonly used in NRUS experiments. It will be shown that $\alpha_E$ in progressively damaged samples does increase with the corrosive environment exposure time and that NRUS can be used to quantify the cumulative amount of damage by measuring $\alpha_E$. Thus here we are measuring $\alpha_E$ instead of the beta parameter associated with second harmonic generation as was used by Morlock et al. and we exposed more samples to a corrosive environment for different lengths of time that they did. The purpose of this study is not to provide a direct forecast of the $\alpha_E$ expected for a given exposure time of SCC accumulation in storage casks since the corrosion process for storage casks is much slower than the one used here. Rather this paper indicates that there is an exponential increase in $\alpha_E$ with exposure time for the samples studied here and we suggest that an exponential increase would be expected for other systems, albeit with different exponential fit parameters.

2. Sample creation

Samples of 304L stainless steel having a weld and a cylindrical shape were created. The simple cylindrical geometry ensures that individual modes may be identified and excited. The weld provides a HAZ where SCC would most likely develop. No external stress is applied to the samples. The actual samples were created by welding two 6.35 cm (2.5 in.) length pieces to create 12.7 cm (5 in.) long samples. The weld material is 308 stainless steel, the same weld material used for nuclear storage casks. Fig. 1(a) displays a photograph of two virgin samples with the weld and HAZ identified. Usually the samples appear to be welded similarly. Fig. 1(b) displays a photograph of two damaged samples with visible cracks identified by the arrows. Prior to inducing damage in the samples, the fundamental longitudinal resonance frequencies were measured to determine a measure of the consistency in the samples. The mean frequency value was 19.49 kHz and the frequencies ranged from 19.42 kHz to 19.55 kHz, implying that the samples were made in a fairly consistent manner.

To induce SCC, samples are placed in a hot, corrosive environment to accelerate the development rate of cracking. The environment consists of a 42% MgCl$_2$ solution created by mixing tap water with anhydrous MgCl$_2$. The 1 L beaker used to contain the solution is maintained at the 500 mL mark. The solution is heated to 80 °C using a hot plate for the duration of the exposure of the rods to the solution (see Fig. 1(c)). The high temperature causes evaporation, necessitating refilling the beaker. Evaporation is minimized by using a watch glass to mostly cover the beaker, allowing evaporated water to condense on the watch glass and drip back down into the solution. Only water is needed to restore the MgCl$_2$–water ratio, since only the water evaporates. Adding additional MgCl$_2$ causes oversaturation. When samples are removed,
MgCl2 and water are added to maintain the 42% solution since some salt adheres to the removed rods and needs to be replaced. Twelve samples are initially placed in the solution and one is taken out every two days. Fig. 1(d) displays a photograph of 5 of the samples with varying degrees of exposure and visible cracks identified by arrows. Any residual salt that collected on the rods was washed off.

3. Experimental setup

NRUS experiments are controlled and data are acquired using custom LabVIEW software. A stepped sine wave excitation signal is output from a National Instruments PXI-5406 FGEN card (16-bit resolution and 40 MHz sampling frequency). Each step consists of a sine wave that lasts for the duration of the specified 50 ms ring-up and 50 ms acquisition times. This allowed for avoiding the transient ring up and to record approximately 800 cycles of time during the steady state portion of the sample excitation. This signal is amplified using a Tabor Electronics amplifier, model 9400 with a fixed 50 × gain. The amplified signal is sent to a cylindrical, APC International piezoelectric transducer of type 851, with dimensions 15.7 mm diameter by 6.4 mm thickness. The response of the sample is measured by a Polytec PTV-400 Scanning Laser Doppler Vibrometer (SLDV), whose output is digitized with a National Instruments PXIe-5122 digitizer (14-bit resolution and 100 MHz sampling frequency). The laser is shined on the flat end of the cylinder opposite to the piezoelectric transducer (PZT).

The frequency range of the stepped sine wave signal is selected to excite the first longitudinal mode of vibration of the sample. This sample, of mass \( m \) and length \( L \) excited by wavenumber \( k \) can be modeled as having a mass loaded end (with the piezoelectric transducer as the mass load, \( m_0 \)) and a free end,\[
\tan(kL) = -\left(m/m_0\right)kL.
\] (2)

This transcendental equation is used to predict the longitudinal resonances \( [20,21] \). Samples of length 12.7 cm (5 in.) and diameter 1.59 cm (5/8 in.) are found to have longitudinal modes that are sufficiently separated from torsional and flexural mode frequencies that were estimated by assuming free-free bar boundary conditions (experimental measures of the modal frequencies of all three types of modes were in decent agreement).

NRUS data have a frequency resolution of 0.2 Hz. The frequency range used depends on the resonance frequency of the sample under test. Relatively undamaged samples have a frequency range that is slightly wider than the full width at half maximum span of frequencies. More damaged samples require a wider frequency range that extends further below the sample's resonance frequency, because the frequency shift is greater in damaged samples. The sample exposed for the longest time, which is expected to have the most damage, is measured from 14.8 to 15.4 kHz while the undamaged sample was measured from 18.2 to 18.5 kHz. These frequency ranges correspond to the span necessary to capture the resonance frequency peaks at each of the drive amplitudes. The NRUS measurements utilize excitation voltage levels of 10V-100V in increments of 10V output from the amplifier to the transducer.

4. Results and discussion

Fig. 2(a) displays sample NRUS measurements from samples exposed for 6, 14, and 22 days. Once the NRUS data is obtained, a parabolic peak-finding algorithm is used to carefully identify the peaks of the resonance curves, including the frequency at which the peak occurs and the amplitude of the peak. The measured peak amplitudes and resonance frequencies are exported to MATLAB to apply linear curve fitting in order to extract the \( \alpha_E \) of the sample. The relative frequency shift is defined as

\[
\frac{\Delta f}{f_0} = \frac{f - f_0}{f_0},
\] (3)

where \( f \) is the measured resonance frequency (obtained from the peak-finding algorithm) at the \( i \)th excitation amplitude and \( f_0 \) is the lowest amplitude resonance frequency measured. The strain for each resonance curve is calculated by dividing the peak velocity measured (obtained from the peak-finding algorithm) by the sample's longitudinal wave speed \( [5] \). Note that this estimation of the strain is an approximation based on a homogenous sample. Our samples are not homogenous due to the weld material in the middle and because these samples have localized cracking in them. It has been recently shown that the nonlinearity obtained using NRUS is an average estimation of the local nonlinearity driven by the local strain field over the entire sample \( [22] \). The strain, \( \epsilon \), reported should represent values close to those actually experienced in these rods, particularly where the damage appears to be most prevalent, near the weld towards the middle of the sample where the strain is expected to be the largest.

The relative frequency shift values are plotted as a function of the strain and analyzed in MATLAB using a least-squares linear fit to extract the slope of the data. The absolute value of the slope is the measured \( \alpha_E \). Fig. 2(b) displays three sets of relative frequency shift data as a function of strain for the NRUS results displayed in Fig. 2(a) along with the linear fit to each data set. The measured \( \alpha_E \) are 5.80 × 10^2, 2.47 × 10^3, and 1.03 × 10^4, respectively. The respective coefficient of correlation, \( R \), values were 0.992, 0.992, and 0.996.

The process outlined above is followed for 13 samples. Table 1 displays the measured quality factor for the lowest amplitude excitation resonance curve, the effective Young’s modulus calculated from the sound speed in Eq. (2) and the lowest amplitude resonance frequency (assuming the mass of the rods was unchanged), the maximum frequency shift measured at the highest excitation level, the maximum strain induced, the measured \( \alpha_E \), and the \( R \) of the linear fit for each sample. The quality factor changes by a factor of 6.2 and the Young’s

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Nonlinear Resonant Ultrasound Spectroscopy (NRUS) was used to measure the amplitude dependence of the first longitudinal resonance frequency of the samples. The nonlinear parameter, $\alpha_E$, was extracted from the relative shifting of the resonance frequencies, measured as a function of assumed strain levels. It was found that SCC can be induced in a relatively fast manner using lower temperatures than typically used in the literature [23]. It was also found that while there is not a perfect monotonic increasing trend, there still is a general exponential trend between exposure time and the measured $\alpha_E$, which suggests that the NRUS results are likely correlated with the cumulative degree of SCC in a sample. Differences in the data are thought to be due to differences in the welding process when the samples were created. Given the assumptions made, the trend shown in Fig. 3 indicates that higher quantities of SCC damage exhibit larger nonlinear shifts in resonance frequency. Application of this process to detecting SCC in storage casks, or other systems, would require determining the relationship of $\alpha_E$ to exposure time for that specific system, though an exponential increase in $\alpha_E$ with time is expected based on the results shown here.

Acknowledgements

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References


5. Conclusion

Twelve stainless steel samples have been exposed to hot magnesium chloride for different lengths of time ranging from 2 days to 24 days to induce Stress Corrosion Cracking (SCC) in an accelerated manner.


Nonlinearity from stress corrosion cracking as a function of chloride exposure time using the time reversed elastic nonlinearity diagnostic

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The Time Reversed Elastic Nonlinearity Diagnostic (TREND) has a long history of successful non-destructive detection of cracks in solids using nonlinear indicators. Recent research implemented TREND to find stress corrosion cracking (SCC) in the heat-affected zone adjacent to welds in stainless steel. SCC development around welds is likely to occur due to the temperature and chemical exposure of steel canisters housing spent nuclear fuel. The ideal SCC detection technique would quantify the size and extent of the SCC, rather than just locating it, as TREND has been used for in the past. The current paper explores TREND’s ability to detect an assumed increase in SCC over time using 13 samples exposed to a magnesium chloride (MgCl2) bath for different lengths of time. The samples are then scanned with TREND and nonlinearity is quantified for each scan point and each sample. The results suggest that TREND can be used to not only locate SCC in the heat-affected zone, but also track an increase in nonlinearity, and thereby an increase in damage, in samples exposed to the MgCl2 solution for a longer duration. © 2019 Acoustical Society of America.

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I. INTRODUCTION

Time reversal (TR) focusing has been used for the nondestructive evaluation (NDE) of solid media for just over a decade. TR utilizes the reversed impulse response of a system to generate a temporal focus of vibration energy at a single location,1 which can be used to reveal the local system properties upon examination of the focal signal.2 Direct excitation of a cracked location may be insufficient for generation of the amplitudes necessary to allow detection of the nonlinear response of the damage. TR focusing has been shown to generate 30 times higher peak amplitude than direct excitation (though a factor of about 10 is typical), per channel, and therefore has sufficient amplitude to allow detection of local nonlinear properties.3 Analysis of the TR focal signal reveals nonlinear variations in a number of forms including higher signal amplitude, waveform distortions,4,5 or nonlinear harmonic content.6,7 For a focus at a cracked location in a medium, all of these indicators and more typically exist.

The earliest methods utilizing TR for NDE detected scattered waves from a defect as an impulse response that could then be reversed in time and focused at the defect to localize it.8–11 This linear process, called DORT (for the decomposition of the time reversal operator), was used for flaw detection in materials such as titanium and duralumin.12–15 An iterative TR technique was also developed to increase the scattered signal strength.16,17 In solid media, additional linear TR methods have been developed to locate acoustic emissions,18,19 earthquakes,20–23 finger taps,24,25 and linear scatterers.26–28 The use of TR for the nonlinear detection of cracks was proposed by Guyer29 and numerically verified by Delsanto et al.30 and Bou Matar et al.31 Sutin et al.6,7 were able to experimentally confirm a reciprocal TR process where a focus is placed at any location specified by a noncontact receiver, allowing an entire region to be studied without transducer rebonding. Experimental validation of the use of TR for nonlinear detection and imaging of cracks was done for impact damage32,33 as well as stress fatigue34 and delaminations.35,36 In these studies, high-amplitude TR focusing was intentionally used to excite local nonlinearities from damage, and ultimately, a technique termed the Time Reversed Elastic Nonlinearity Diagnostic (TREND) was developed to image damage in a sample.36–38 Additional recent experiments have used nonlinear techniques in conjunction with TR to study closed cracks,39 and use TREND to both locate and study the depth of stress corrosion cracking (SCC) near welds.40–42 An overview and summary of TR techniques for NDE utilizing nonlinear acoustics was recently published.43

The TREND technique excites nonlinearities at a specific location by training a high amplitude TR focus of acoustic energy to that location. A series of scan points is selected in a region of interest and a TR focus is generated.
and measured at each location in turn. In these experiments, the TR focus of energy at a single location, even a cracked one, is still considered to be nondestructive since the strain is kept at least an order of magnitude smaller than the linear strain relationships of the undamaged medium. By evaluating each scan point’s focal signal for nonlinear content, a visual map of the quantified nonlinear signature is produced wherein high amounts of nonlinearity are assumed to imply more damage. Because every hardware system inherently generates some level of nonlinearity, assessments of nonlinearity correlated to damage should be made relative to a measurement at an undamaged location in the sample or to an undamaged sample. This relies on a clear distinction between system and sample nonlinearity, a sometimes difficult requirement not always necessary for linear detection systems. The success of TREND is partially due to its localized, high focal amplitude, which makes system noise less of a problem. In addition, studies have shown that nonlinear detection methods like TREND are able to find damage at a very early stage,\(^{44}\) as opposed to linear acoustic techniques (e.g., pulse echo) that tend to detect the damage once the system is close to failure.

Recent research investigated the use of TREND for nondestructive localization and characterization of SCC with application to steel canisters holding spent nuclear fuel.\(^{30,42,45}\) The approximately 3.7 m (12 ft) diameter cylindrical canisters are air-tight and are surrounded by a cylindrical concrete cask with air vents. These canisters are often stored near coastlines. Due to internal heating and a cool exterior, the salt-air exposure, and residual stresses, SCC may develop near welds. Long exposure to these conditions might lead to SCC beginning to threaten the air-tight seal.\(^{46–48}\)

The development of SCC around welds occurs as a result of residual stress and long-term exposure to moist, chloridic environments.\(^{39}\) In austenitic stainless steels, like those used for nuclear fuel storage canisters, the necessarily high heat associated with the welding process adjusts the structure of the steel adjacent to the weld, allowing the base steel to bond to the weld filler material, but also potentially weakening the crystalline framework of the base steel. The steel altered by the heat of welding is called the Heat-Affected Zone (HAZ). After cooling, the HAZ can often be roughly identified by external discoloration caused by oxidation of the steel adjacent to the weld,\(^{30}\) although it is impossible to know the true extent of the HAZ without high resolution imaging of the grain structure.\(^{51}\) Within the HAZ, the grain boundaries at the transition between the base and filler metals can result in a residual stress from the welding process. Given ongoing exposure to high temperatures, humidity, chlorides, or any service-induced stress, SCC is most likely to form within the HAZ, especially along the edge of the weld.\(^{42,49}\) An example of SCC in stainless steel is shown in Fig. 1 with labels indicating the weld, HAZ, and SCC.

In the study conducted by Anderson et al.,\(^{40}\) a sample of 304L stainless steel (the subject of the photograph in Fig. 1), the same steel used in the storage canisters, was welded and subject to a boiling magnesium chloride (MgCl\(_2\)) bath to induce SCC in the HAZ. Imaging nonlinearity along the weld with TREND identified not only the location of SCC, but also discovered clues concerning the depth dependence of the cracking by using various frequency bandwidths for measurement. The external concrete encasing the steel canisters makes inspection difficult, but the TREND method may be employed in the intentional gap (for air flow) left between the steel canister and concrete cask making it possible to inspect SCC without disturbing the protective barriers.

A number of other nonlinear ultrasound techniques aimed at NDE of SCC have been used in the past. Ohara et al.\(^{52}\) used a Subharmonic Phased Array to detect frequency mixing by SCC on the opposite side of a sample from the transducer or on the same side of the sample.\(^{53}\) Dynamic Acousto-Elastic Testing was used to compare time-of-flight measurements across a dynamically strained crack.\(^{54}\) Nonlinear Resonant Ultrasound Spectroscopy was used to locate SCC from resonance frequency shifts observed for different modes of a globally excited sample.\(^{55}\) Morlock et al.\(^{56}\) used Rayleigh waves to excite SCC which are then detected downstream of the crack. This last experiment was the only one to use multiple samples with differing degrees of SCC, which were induced by applying differing amounts of stress to samples exposed to a corrosive environment for the same amount of time. So far, there has not been a published study that exposed several samples to a corrosive environment for differing amounts of time nor a study exposing one sample to corrosion, monitoring it, and then exposing it again and repeating this cycle. This work does the former, exposing multiple samples to corrosion for differing amounts of time. Some of the above techniques were designed for advanced laboratory studies and not for field work (e.g., Dynamic Acousto-Elastic Testing), and some cannot easily localize SCC (e.g., Nonlinear Resonant Ultrasound Spectroscopy).

Developing TREND to be a robust tool for detecting and imaging of SCC for field testing is desired, meaning the ability to detect the depth of SCC and the orientation of the SCC. This information could allow corrective action to be taken before the air-tight seal is compromised. The purpose

![FIG. 1. (Color online) An image of 304L stainless steel with SCC in the HAZ just outside the weld. In this case, SCC has developed in the HAZ and occasionally in the weld.](Image 330x563 to 546x765)
of this paper is to experimentally study the ability of TREND to locate SCC in the HAZ of welds, but more importantly, correlate the amount of measured nonlinearity to the assumed amount of SCC present. By exposing a number of identically welded steel samples to a hot MgCl$_2$ solution for varying amounts of time, a series of samples are created with an expected, successive increase in SCC with longer exposure time. Using TREND, each of these samples is nondestructively examined and it is found that, with some variation, the longer a sample is exposed to the solution of MgCl$_2$, the more nonlinearity is measured in the HAZ.

The paper first describes the details of TREND processing, including the details of the system used, and experimental specifications. This will be followed by a description of the samples as well as the process for inducing SCC in the HAZ of each sample. Results of nonlinear imaging of cracks will be shown in detail for a representative sample after which the overall nonlinearity for each sample will be calculated and plotted against the exposure time of the sample to the hot MgCl$_2$ solution.

II. EXPERIMENTAL SETUP

TR utilizes the impulse response between a source and receiver to create a focus of energy at a selected location.$^{1,2}$ In the so called forward propagation step, an acoustic impulse is sent from a source, which propagates throughout the medium including multiple reflections and scattering, and is recorded by a receiver as the impulse response. In standard TR, the impulse response is reversed in time and emitted from the original receiver location. In this backward propagation step, the emitted waves constructively interfere to generate a focus of acoustic energy at the original location of the source during the forward step. If reciprocity can be assumed in the medium, the time-reversed impulse response can instead be emitted from the source location during the backward step to generate a focus at the receiver location. This method is termed reciprocal TR and utilizes the convenience of a source emitter that remains in place during the forward and backward steps.$^{57,58}$ In applying reciprocal TR to nonlinear detection of damage, a non-contact receiver allows a system to be trained to focus at multiple locations without moving the sources and provides a simple and quick method for imaging nonlinearity.

A PSV-400 Polytec (Walldbronn, Germany) scanning laser Doppler vibrometer (SLDV) provides a noncontact receiver to measure out-of-plane velocity on the sample surface and eight piezoelectric transducers (from APC International located in Mackeysville, PA, material type 850), measuring 19.0 mm in diameter by 12.0 mm in thickness, generate the source signals. In practice, a truly impulsive waveform is difficult to generate with band-limited piezoelectric transducers. Therefore, a linear chirp signal, like that shown in Fig. 2(a) (where the frequency content has been altered for visualization purposes), is utilized as the source signal for the forward propagation step, and a chirp response, shown in Fig. 2(b), is collected at the receiver in lieu of an impulse response.$^{59,60}$ The chirp signal is cross correlated with the chirp response in order to determine the required reversed impulse response [see Fig. 2(c)]. The reversed impulse response is sent through the sample from the band-limited transducer to the receiver generating a focus of energy, an example of which is shown in Fig. 2(d). This chirp method both increases the total energy input to the system during the forward step and recognizes bandwidth limitations of transducers by utilizing a finite bandwidth source signal. The fundamental bandwidth is defined by the span of frequencies used in the chirp signal. Higher harmonic bands generated by nonlinear vibration are defined as integer multiples of the fundamental bandwidth.

Samples containing SCC in 304L stainless steel are created through exposure to a hot chemical bath.$^{61}$ Thirteen rods of length 12.7 cm (5 in) and diameter 1.59 cm (5/8 in) are cut in half along the length of the rod and then welded back together with a “V-groove” weld using 308 weld material, as shown in Fig. 3(a). One of the rods is left untouched while the remaining 12 rods are exposed to a 42% MgCl$_2$ bath at 80°C [see Fig. 3(b)]. One rod is removed from the solution every two days, such that the shortest exposure time is two days and the longest is 24 days. An example of one of the rods exposed to MgCl$_2$ for 14 days is shown in Fig. 3(c), although SCC is not visually apparent. Water is added to the solution to maintain a consistent salinity as needed.

One at a time, a rod is epoxied to the top of a steel disk of diameter 20.2 cm (8 in) and height 2.5 cm (1 in), which is elevated by three rubber mounts 2 cm (0.79 in) above an optical table. Eight piezoelectric transducers are epoxied to the underside of the steel disk. Relative to the center of the disk, transducer 1’s center is at a radius of 5.8 cm and located at 0°, transducer 2’s center is at a radius of 5.3 cm and located at 34°, transducer 3’s center is at a radius of 5.4 cm and located...
at 74°, transducer 4’s center is at a radius of 5.7 cm and located at 103°, transducer 5’s center is at a radius of 5.5 cm and located at 158°, transducer 6’s center is at a radius of 4.8 cm and located at 197°, transducer 7’s center is at a radius of 4.1 cm and located at 252°, and transducer 8’s center is at a radius of 5.2 cm and located at 291°. Because nonlinear increases to harmonic amplitudes can be difficult to detect without sufficiently high amplitude excitation, TR focusing from each of the eight transducers are simultaneously superposed to create a focus at a single location. Placing eight transducers on the rod itself is both inefficient given the curved rod surface and can physically block access to a cracked location. Therefore, the energy from the transducers is transmitted through the disk and into the rod. The disk creates a so-called chaotic cavity to increase diffuse reverberation in the impulse responses. The epoxy bond between the disk and rod is an average of 0.79 mm in thickness and care is taken to make the bond both consistent between rods and level such that the disk and rod do not have direct contact, thereby avoiding contact nonlinearity. The bond is given 36 h to cure before testing takes place. An image of a rod epoxied to the disk is shown in Fig. 4.

The nature of NDE of samples implies that the exact extent of any damage in the samples is truly unknown. While it is supposed that cracking will occur in the HAZ, the HAZ itself is a tenuously defined region, and damage could exist anywhere along the circumference of the rod. Thus a 50 mm scan is conducted along four lines of scan points with each line spaced apart by 90° angles around the rod. Between each measurement along a given scan line on a rod, the steel disk and sample setup is rotated by 90°. The SLDV is positioned to provide very close to normal incidence sensing of surface vibration (along the length of the rod) throughout the scan.

During the forward propagation step, the chirp signal is broadcast from one source transducer at a time and the response is recorded by the SLDV at the current scan point. Each of the eight impulse responses between the eight source transducers and the current scan point are obtained as described previously. These impulse responses are reversed in time and amplified to the maximum output available from the amplifier. Each of the eight reversed impulse responses provides a TR focus at the current scan point that constructively interfere. The SLDV records the focal signal at this current scan point. The SLDV is then positioned at the next scan point and the entire process, described in this paragraph, is repeated. Thus, TR focusing occurs at the location where the SLDV is aimed during the forward propagation step.

III. RESULTS

Two focal signals are shown in Fig. 5 for illustrative purposes. Both of these signals come from the same rod exposed to MgCl₂ for 12 days and both are within the supposed HAZ, but Fig. 5(a) is the focal signal from a location 14.2 mm from the outer edge of the weld and Fig. 5(b) is only 2 mm from the weld. The first attribute of note, relative to many other TR experiments is the large temporal side lobes on either side of the peak focus. While some applications of TR require a more delta-function like focal signal, this is less important for crack detection. The high-amplitude side lobes in the focal signal imply that this system is a highly resonant one; in fact, spectral analysis suggests there are several sample resonance modes within the...
the frequency band used in the experiment. The most important aspect of TR focusing for nonlinear detection is the amplitude of the signal, which triggers a nonlinear response and allows detection of nonlinear features (i.e., harmonics). Figure 6 shows the spatial distribution of the instantaneous velocity along the rod at the moment of TR focusing on an unexposed rod. The "×" symbol indicates the location of the focus as well as its amplitude at the focal-time. Examination of this figure indicates an average wavelength of 26 mm. Using the central excitation frequency of 100 kHz, the wave speed is calculated as 2600 m/s, a value close to the expected Rayleigh wave speed of 2860 m/s in 304L steel. TR inherently utilizes all types of propagating waves (i.e., propagation modes) present in a system. The authors expect that the waves used to generate focusing in the rod are likely dominated by antisymmetric (so called A0) lamb waves and torsional waves.

Potential nonlinearity in the focal signals, due to the presence of damage, is quantified from Fourier transforms of the signals in Fig. 5, shown in Fig. 7, and labeled with their distance from the outer edge of the weld. A comparison of the two signals on the same amplitude scale, shown in

![FIG. 5. (Color online) Time-domain focal signals from two scan points on the rod exposed to magnesium chloride for 12 days. (a) Focal signal 14.2 mm from the weld. (b) Focal signal 2 mm from the weld.](image1)

![FIG. 6. (Color online) Instantaneous velocity along the length of rod at the moment of time reversal focusing on an unexposed rod. The focus is generated at the location marked by the ×.](image2)

![FIG. 7. (Color online) Spectra of the focal signals displayed in Fig. 5. Amplitude scaling to the Euclidean norm of the spectra within the fundamental bandwidth is applied, shown mathematically in Eq. (1). The fundamental bandwidth is outlined by the vertical dash-dot lines. The second harmonic is outlined by the vertical dashed lines.](image3)

\[
\|G(f)\| = \frac{G(f)}{\sqrt{\sum_{75 \text{ kHz}}^{125 \text{ kHz}} G^2(f)}}.
\]
150 to 250 kHz, is outlined in dashed vertical lines in Fig. 7 and comprises the region most likely to indicate the presence of nonlinearity introduced by crack motion. Other harmonics were examined but were buried in the noise floor. If the localized focus of energy excites SCC, the crack produces harmonics of the fundamental. The higher the amplitude of the spectra in the second harmonic relative to the fundamental amplitude, the larger extent of SCC is expected. In Fig. 7, the two signals have approximately the same amplitude within the fundamental bandwidth, as expected given the applied scaling, although both have multiple peaks due to the resonances of the sample and source transducer. However, within the second harmonic band, the amplitudes for the spectrum corresponding to the location 2 mm from the weld are distinctly higher in amplitude than in the spectrum for the 14.2 mm distance from the weld, indicating a higher severity of damage. This result is expected given that SCC is more likely to form immediately just adjacent to the boundary of the weld; nevertheless, both positions are within the HAZ and an examination of the entire spatial region is necessary to see the impact of a variety of differences in the second harmonic amplitude.

Nonlinearity across the entirety of a scan line is compared after the amplitude in the second harmonic is reduced to a single number. This is accomplished by calculating the scaled nonlinearity

\[ \zeta(x, \theta_n) = \frac{1}{500 kHz \cdot 250 kHz} \sum \| G(x, \theta_n, f) \|^2, \]

where the spectral amplitudes within the scaled second harmonic bandwidth are squared and summed for each scan point, \( x \), and at the rotation angle, \( \theta_n \). The higher the scaled nonlinearity, the more likely SCC has developed at location \( x, \theta_n \). The scaling of the focal spectra and comparison of relative amplitudes of the second harmonic is similar in nature to the frequency domain scaling subtraction method, but the scaling used here is based on the fundamental bandwidth of each spatial scan location rather than comparing a high-amplitude focal spectrum to a low-amplitude focal spectrum.

Scaled nonlinearity, \( \zeta(x, \theta_n) \), results are shown in Fig. 8 for the rod exposed to MgCl\(_2\) for 12 days. The four plots in Fig. 8 indicate the results from each of the four \( \theta - \) angles 0°, 90°, 180°, and 270° in Figs. 8(a), 8(b), 8(c), and 8(d), respectively, scanned on the rod. The horizontal axis shows the scan position, \( x \), in millimeters with distances relative to the top of the rod (the end not epoxied to the disk). The vertical axis shows the scan position, \( x \), in millimeters with distances relative to the top of the rod (the end not epoxied to the disk). The vertical axis shows the scan position, \( x \), in millimeters with distances relative to the top of the rod (the end not epoxied to the disk). The vertical axis shows the scan position, \( x \), in millimeters with distances relative to the top of the rod (the end not epoxied to the disk).

Because the results depicted in Figs. 8(a)–8(d) all display peaks in \( \zeta(x, \theta_n) \) just adjacent to the weld, it could be thought that what is detected is not nonlinearity from SCC at all, but merely odd behavior due to the edge of the weld. However, the data for the rod that was not exposed to the MgCl\(_2\) but had the same size and shape (rod exposed for zero days). Data are from a 200 point scan at \( \theta = 0° \), (b) 90°, (c) 180°, and (d) 270°.
MgCl$_2$ solution is also shown in each of these figures, and no spikes are observed at the edges of the welds in that sample. Some features exist at levels of $\zeta = 10^{-5}$ in the unexposed rod; however, these features are inconsistent spikes indicative of noise and occur at random locations on the rod, both near and far from the weld. Therefore, we assert that the nonlinearity detected in the exposed rods is due to SCC, and not the weld boundary.

NDE techniques utilize both linear and nonlinear metrics to detect damage. One might expect that severely damaged locations (open cracks) would possess high peak focal amplitude, as the excited crack is more freely able to vibrate at an open crack boundary than material constrained within a homogeneous medium. Thus, the fundamental bandwidth is expected to have higher amplitudes and the peak focal amplitude would be higher. In the research shown here, the two focal signals shown in Fig. 5 indicate that the rods not only constitute resonant systems, but that the highest focal amplitude did not correspond to the location where SCC is likely to exist, since the damaged location yielded a lower peak focal amplitude. Figure 9 illustrates the resonance characteristics of the rod more clearly by showing the peak focal amplitude, $A_p$, in mm/s of each independently generated focal signal on the left vertical axis plotted against $x$, and $\zeta(x, \theta_n)$ from the same data set on the right axis, also plotted versus $x$. The scan data are the same as that shown in Fig. 8(d). The peak focal amplitude ranges from 54 to 76 mm/s, and oscillates with an average peak to peak distance of 28 mm, a distance within 2 mm of the wavelength determined from the plot in Fig. 6. Notably, the peak focal amplitude is highest where $\zeta(x, \theta_n)$ is not. There is some indication that damage has an impact on focal amplitude, such as the matching peaks at $x = 54.6, 57.6$, and 67.2 mm. However, these minor peaks in focal amplitude are more likely to look like false detections than cracks if one were basing crack detection solely on the peak focal amplitude, when comparing those minor peaks to the large amplitude gains at $x = 48, 62$, and 76 mm. While an increase in peak focal amplitude may be a valuable linear indicator of damage for some varieties of cracking, it is apparently not sufficient for SCC in a resonant system, and could lead to erroneous results. This result indicates the importance of NDE imaging based on nonlinearities generated by cracking. In addition, given the wavelength of 26 mm, the defects should only be detected if they are larger than the half-wavelength diffraction limit of 13 mm. However, nonlinear cracking features appear to be discernable in regions as small as 5 mm. Though beyond the scope of this paper, this could be the result of the diffraction limit of the second harmonic used, approximately 6 mm.

Of the 12 rods exposed to MgCl$_2$, ten showed evidence of nonlinearity in the HAZ, especially adjacent to the weld. The two that did not were only exposed for two days and four days. To compare the total damage in the rods, all of the localized and scaled nonlinearity ($\zeta(x, \theta_n)$) like that shown in Fig. 8 must be quantified for each rod. Because each focal spectra is scaled to the amplitude of its fundamental bandwidth, differences in focal amplitude (which is dominated by the fundamental frequency bandwidth) between the rods has no impact and only the relative height of the second harmonic, the scaled nonlinearity, is used as a damage indicator. The entire length of the scan is used to quantify a total nonlinearity for each rod because, as was evident in Fig. 8, not all spikes in $\zeta(x, \theta_n)$ occur adjacent to the weld, and all nonlinearity should be accounted for. To determine the total nonlinearity, $Z(\theta_n)$, for each rotation angle on each rod, the $\zeta(x, \theta_n)$ values for each of the 200-point scans are averaged

$$Z(\theta_n) = \sqrt{\frac{1}{200} \sum_{n=1}^{200} \zeta(n, \theta_n)}. \quad (3)$$

The values at each angle $\theta_1, \theta_2, \theta_3, \theta_4 = 0^\circ, 90^\circ, 180^\circ, 270^\circ$ are then averaged to determine one value of total nonlinearity for each rod, $Z$.

$$Z = \sqrt{\frac{1}{4 \times 200} \sum_{\theta_n=1}^{\theta_4} \sum_{n=1}^{200} \zeta(n, \theta_n)}.$$

$Z$, along with the four $Z(\theta_n)$ values, are plotted versus the amount of time each rod is exposed to the hot MgCl$_2$ solution in Fig. 10. The rods exposed from zero to four days have total nonlinearity values that are very low and essentially negligible. For the rods exposed from six to 24 days, various amounts of nonlinearity are detectable and there is an overall increase in $Z$ with exposure time. Notable exceptions to this trend are the rods exposed for 10, 16, and 20 days, which show surprisingly low $Z$ given their exposure time. However, because welding is not an exact process, it is not known whether these rods had very little residual stress compared to their peers in the regions examined. It is also possible that the four angles examined on these rods simply missed whatever SCC was present within the rods. Studying a larger set of samples would determine the expected amount of variance in this trend of $Z$ versus exposure time. The data is erratic particularly from the sample exposed for 14 days to the sample exposed for 20 days. However, the general

![FIG. 9. (Color online) Left axis: peak focal amplitude, $A_p$, versus scan position, $x$. Right axis: scaled nonlinearity, $\zeta(x, \theta_n)$, versus scan position. The outer edges of the weld are indicated by the vertical dashed lines.](image-url)
increase in $Z$ with exposure time suggests that TREND can be used to track SCC progression over time on similar samples and need not be a measurement system limited to measurements on a single sample. Given this result, TREND could be utilized on storage casks to determine the extent of SCC growth. However, the nonlinearity observed over the short exposure times used here would not be expected to translate to actual casks because the corrosive environment for storage casks is not nearly as severe.

It is worth noting that a parallel study was conducted by Hogg et al. (many of the authors of this paper) using nonlinear resonant ultrasound spectroscopy on these same samples to measure the amplitude dependent frequency shift of the fundamental longitudinal mode in the samples. These results also did not show any significant increase in the measured nonlinearity in the virgin sample and the samples exposed for two and four days. The samples exposed for longer time generally showed an increase in nonlinearity with increasing exposure time; however, the samples exposed for 10 and 20 days each had significantly lower measured nonlinearity in them as would determined in the present paper. The sample exposed for 16 days also showed a significant drop in $Z$ in this paper, but a similar drop was not observed by Hogg et al.

IV. CONCLUSION

Thirteen stainless steel rods were cut in half and welded back together and exposed to a solution of hot magnesium chloride for varying amounts of time. Using TREND, each of the rods was scanned, placing a high-amplitude focus of energy at each scan location, and the nonlinear content in the second harmonic was quantified in the scaled focal signals. It was found that the focal signals of scan points adjacent to the outer edge of the weld overall contained more nonlinearity, an expected result given the propensity of these regions to SCC being located within the heat-affected zone. Additionally, the maxima of the focal signals, a linear imaging quantity, at each scan location could not be used to identify locations with SCC. A value for total nonlinearity was quantified for each rod, and it was found that, in general, the longer a rod was exposed to the hot solution of magnesium chloride, the more nonlinearity was detected. Thus, this paper illustrated that SCC around welds can not only be detected using TREND, but the nonlinear signature measured with TREND increases with the expected amount of SCC from longer exposure to corrosive environments.

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A comparison of impulse response modification techniques for time reversal with application to crack detection

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Running title: Time Reversal Optimization for Nondestructive Evaluation
ABSTRACT

Time reversal (TR) focusing used for nonlinear detection of cracks relies on the ability of the TR process to provide spatially-localized, high-amplitude excitation. The high amplitude improves the ability to detect nonlinear features that are a signature of the motion of closed cracks. It follows that a higher peak focal amplitude, than what can be generated with the traditional TR process, will improve the detection capability. Modifying the time-reversed impulse response to increase the amplitude of later arrivals in the impulse response, while maintaining the phase information of all arrivals, increases the overall focal signal amplitude. A variety of existing techniques for increasing amplitude are discussed, and decay compensation TR, a technique wherein amplitude is increased according to the inverse of the amplitude envelope of the impulse response decay, is identified as the best modification technique for nonlinear crack detection. This technique increases the focal signal amplitude with a minor introduction of harmonic content, a drawback in two other methods studied, one-bit TR and clipping TR. A final study employs both decay compensation TR and traditional TR focusing on a rod with stress corrosion cracking and compares the merits of each in detecting nonlinearity from cracks in a real system.

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I. INTRODUCTION

The time reversal (TR) process utilizes the impulse response of a system, between a source and a receiver, to generate both a spatial and temporal focus of energy at a chosen location.\(^1\) The impulse response is reversed in time and then emitted by the source (reciprocal TR\(^2\)) with the low-amplitude vibrations emitted first and the high-amplitude vibrations last. The timing of the emitted waves is determined by the reversed impulse response (RIR). For a time-invariant system, each of the emitted waves travels along the paths traversed during the impulse response measurement and the timing is such that energy from each emission arrives simultaneously at the receiver location, creating a constructive focusing of energy that is generally impulsive in nature.

The TR focus of energy has been utilized for nondestructive evaluation (NDE) (i.e. crack localization) since the early 1990s, for example with Chakroun et al. using TR to locate scatterers in a solid sample submerged in a fluid.\(^3\)-\(^5\) In 2001, Guyer first proposed using high-amplitude TR focusing for nonlinear imaging of cracks\(^6\) and Ulrich et al. demonstrated this experimentally a few years later by locating a surficial crack in a doped glass sample.\(^7\) Studies since then have used TR to find nonlinearity in various types of surface cracks,\(^8\)-\(^11\) near-surficial cracks and delaminations,\(^12\)-\(^13\) and even buried cracks.\(^12\),\(^14\) The detection of cracks using nonlinear methods is rooted in the premise that cracks will generate nonlinear frequency mixing when excited with sufficient amplitude.\(^15\)-\(^16\) It has been shown that nonlinear methods detect damage sooner than their linear counterparts.\(^17\) TR focusing at a damaged location results in the generation of higher harmonic frequency content. Thus, nonlinear detection methods require a high signal-to-noise ratio (SNR) such that higher-order harmonics are not buried in the noise floor.\(^18\) While TR focusing inherently generates high-amplitude energy focusing, traditional TR signal processing may not be the optimal technique for nonlinear detection of cracks in otherwise isotropic media. A review of
the use of TR techniques to detect nonlinear acoustic features for nondestructive evaluation was recently published by Anderson et al.\textsuperscript{19}

Modifications to traditional TR processing have been studied in a variety of contexts. One-bit TR was developed by Derode \textit{et al}. as a method of increasing the amplitude of TR focusing, a technique later explored for use in lithotripsy.\textsuperscript{20-21} Others have used similar techniques wherein the instantaneous amplitude of the impulse response as time progresses is increased to compensate for the natural decay from geometric spreading losses and propagation losses in attenuating media, thereby increasing the SNR of an impulse response in strongly attenuating media.\textsuperscript{22-24} Deconvolution TR, or inverse filtering, was introduced as a means of compensating for resonances in the impulse response to optimize the impulsive nature of a TR focus of energy.\textsuperscript{25-26} Studies have examined the reliance of focal amplitude on the length of the initial pulse (i.e. the bandwidth).\textsuperscript{27-29} Physical system adjustments have sought to increase SNR through other means such as the introduction of a chaotic cavity\textsuperscript{30-33} or the use of an acoustic metamaterial-based filter.\textsuperscript{34} Recently Willardson \textit{et al}. published experimental research manipulating TR processing in order to maximize focal amplitude of audible sound in a reverberation chamber.\textsuperscript{24}

The work by Willardson \textit{et al}. experimentally compared five different techniques that adjust the RIR to ultimately determine which provided the highest peak focal amplitude. The study was conducted in a reverberation chamber using a loudspeaker and a microphone, constituting a wide bandwidth system, and examined various attributes of the focal signals, including peak focal amplitude and temporal quality. While this study was valuable for a thorough understanding of TR in air, the study may not contribute information relevant to crack detection in a solid with a fairly resonant system, as is common for NDE experiments. This paper includes frequency analysis of
higher harmonic generation and an evaluation of the spatial quality of the TR focusing, something that Willardson et al. did not explore.

While previous research has successfully developed modifications of RIR signal processing techniques based on specific targeted outcomes, a comparison of each of these modification techniques with application to NDE has not been done, nor have the impacts of these techniques on the introduction of harmonic frequency content been quantified (many of these techniques are inherently nonlinear processes). Typical solutions for generating the necessarily high SNR in focal signals used in crack detection can require the use of many generation channels or signal amplification beyond the linear limits of the system. The ideal solution to maximize SNR would maintain the physical system but optimize available amplification through the processing of the RIR(s) to increase excitation amplitude at the focus without unduly introducing noise at higher harmonic frequencies or undermining the benefits of using TR for nonlinear crack detection (i.e. spatially compressed focusing).

The objective here is to determine the TR signal processing technique that delivers the largest peak focal amplitude in conjunction with the best temporal quality, a spatially confined focus, and low higher harmonic generation. The purpose of this paper is to experimentally compare five different TR signal processing techniques: deconvolution TR, one-bit TR, clipping TR, decay compensation TR, and as a benchmark, traditional TR, to determine the processing technique best suited for detection of cracks using nonlinear analyses. In this study, it is found that decay compensation TR is the optimal choice for the highest focal amplitude coupled with low higher harmonic generation. It is then shown that decay compensation TR is less susceptible to noise and false detections than traditional TR in the detection of cracks.
The remainder of the paper first describes the experimental setup followed by a description of each of the TR techniques explored. This is followed by a description of the analysis metrics used to compare the methods, peak focal amplitude, temporal quality, spatial quality, and fundamental to higher harmonic ratios. The results are presented for all the TR techniques tested, with some techniques tested with different applied thresholds. Finally, a study is presented that compares the use of traditional and decay compensation TR to find stress corrosion cracking in a steel rod.

II. TIME REVERSAL AND EXPERIMENTAL SETUP

The TR process consists of two steps, a forward step and a backward step. The forward step consists of finding impulse responses from one or more sources to one or more receivers. Typically, an impulse is broadcast from each source and the response is recorded with each receiver to obtain the impulse response(s). In the backward step of the traditional TR process, each impulse response is simply reversed in time and emitted from the receiver. In a variation called reciprocal TR, the RIRs are broadcast from the original source locations, generating a focus of energy at the receiver location(s).

For the experiments described in this paper, a different method is utilized to obtain the impulse responses. First, the broadcast of a true impulsive signal is difficult, from a practical standpoint, for finite-bandwidth transducers. These emissions typically generate low amplitude waves, meaning the SNR of the impulse response is poor. Instead a finite-bandwidth, linear chirp signal is used as the source signal, an example of which is shown in Fig. 1(a). The chirp signal broadcast, being band limited, is efficiently broadcast from transducers and therefore it affords a higher SNR recording than the recording of the response to an impulsive broadcast. The chirp
response is recorded by the receiver and is then cross correlated with the original chirp signal as an approximate means to obtain the impulse response (see Figs. 1(b)-(c)). The impulse response is then reversed in time (Fig. 1(d)) and is broadcast from the same source as the chirp signal (reciprocal TR). The TR focus, shown in Fig. 1(e), occurs at the receiver. This allows the source transducers to be bonded in place and a focus of energy may be generated wherever the receiver is placed.

FIG. 1. Example signals used in the time reversal process. Except for (e), the amplitudes are normalized and are in arbitrary units. (a) Source chirp (with frequencies altered for visualization), (b) chirp response, (c) impulse response, (d) reversed impulse response, (e) focal signal.
The experimental setup, depicted in Fig. 2, is comprised of a steel disk measuring 20.2 cm (8 in) in diameter and 2.5 cm (1 in) in thickness, which is elevated by 3 rubber stoppers 2 cm (0.8 in) above an optical table. A piezoelectric transducer (from APC International located in Mackeyville, PA), material type 850, with diameter 19 mm and thickness 9.5 mm, is epoxied to one side of the disk and operates as the source in both the forward and backward propagation steps. The steel disk is placed with the piezoelectric facing downward toward the table. A PSV-400 Polytec (Waldbronn, Germany) Scanning Laser Doppler Vibrometer (SLDV), a noncontact and mobile receiver, is mounted approximately 1 m directly above the disk with the laser aimed at a patch of retroreflective tape on top of the steel disk. The forward propagation step uses a burst chirp broadcast from the Polytec generator with an amplitude of 0.5 V that is amplified by a Tabor (Nesher, Israel) 9400 high-voltage amplifier, with a 50 times gain, and is input to the piezoelectric transducer. To utilize the piezoelectric transducer efficiently, a chirp bandwidth of 75-125 kHz is chosen, centered on the transducer’s primary radial resonance frequency, and is broadcast for the first half of a 51.2 ms period. A sampling frequency of 1280 kHz, with $N = 65536$ sample points, and a laser sensitivity of 25 mm/s/V is used. It was found that 30 averages sufficiently reduced noise in the system allowing these settings to be used for both the forward and backward propagation steps. After the impulse response is measured it is normalized and reversed in time. Any additional signal processing techniques, such as one-bit or clipping TR, are then implemented and the resultant signal is broadcast into the steel disk, creating a focus at the location where the SLDV measured the impulse response.
FIG. 2. (color online) Experimental setup with scanning laser Doppler vibrometer (SLDV) pointed at a steel disk. The steel disk has a piezoelectric transducer (PZT) epoxied to the bottom.

In an additional experiment, a focus is generated at a single location on the steel disk for each of the signal processing techniques and the wave field is scanned with the SLDV. This gives a spatial map of the velocity at and around the focal location, allowing the spatial extent of the focus to be quantified. For these spatial scans, a region of the steel disk 72 mm x 60 mm in size is covered with retro-reflective tape and a scan grid of 51 points x 43 points is defined, giving a spatial resolution in each dimension of approximately 1.4 mm. A focus is generated at scan position (37, 33.5) mm and the focus is repeated at this location as the SLDV measures the velocity at each scan position.
Deconvolution TR, or inverse filtering, is the first technique optimized to apply to the impulse response. Deconvolution TR inverts the spectrum of the impulse response such that when the resulting RIR is broadcast, the system resonances and antiresonances are compensated for in the backward propagation, yielding a focal signal with nearly a flat frequency response. In practice, deconvolution TR takes the spectrum of the impulse response, $R(\omega)^*$, where the $*$ symbol denotes a complex conjugation, and normalizes it by its squared magnitude plus a scaling factor, $\gamma$, multiplied by the mean of the squared magnitude, as shown in Eq. (1),

$$R_{\text{deconv}} = \frac{R(\omega)^*}{|R(\omega)|^2 + \gamma \text{ mean}(|R(\omega)|^2)}.$$  

The term $\gamma \text{ mean}(|R(\omega)|^2)$ is a regularization term used to keep the deconvolution TR operation finite, a process described in more detail by Anderson et al. Optimization of $\gamma$ for reduction of the energy on either side of the peak focusing (termed side lobes) followed the process described by Willardson et al. and determined an optimal $\gamma$ value of 0.9, which was also the value reported by Anderson et al. for TR focusing of waves in solid media. As $\gamma$ approaches infinity, the deconvolution TR process returns a traditional RIR because the $\gamma$ term dominates in the denominator of Eq. (1) and after normalization, Eq. (1) returns $R(\omega)^*$. As $\gamma$ approaches zero, the impulse response begins to look more like an impulse, effectively eliminating the reverberation in the impulse response. The modified RIR, after the deconvolution TR operation and with $\gamma = 0.9$ is shown in Fig. 3(b).

The one-bit TR technique alters the amplitude of the normalized RIR, $r(-t)$, according to the relationship of the instantaneous amplitude compared to a user-defined threshold (see Fig. 3(c)). The threshold is applied at a positive value $T_{OB}$ and at a negative value $-T_{OB}$. At time sample $t_i$, if $|r(-t_i)| \geq T_{OB}$, then $r(-t_i) \equiv \text{sign}(r(-t_i)) \cdot T_{OB}$. In other words, any signal above or
below the positive or negative threshold, respectively, is set equal to the threshold (or the negative threshold) which is 0.2 in Fig. 3(d). If $|r(-t_i)| < T_{OB}$, then $r(-t_i) \equiv 0$. The quantity $r(-t)$ is then normalized and the resulting modified impulse response is comprised of +1, -1, and 0 values, hence the name one-bit TR (see Fig. 3(e)). The purpose of one-bit TR is to amplify low amplitude reflections in the impulse response and zero-out information with a poor SNR, but maintain the phase information of the non-zero signal. The threshold can be set anywhere from zero to one, thereby defining the acceptable SNR.

FIG. 3. (color online) Impulse response modification techniques with each starting with a traditional RIR, (a)-(b) deconvolution TR, (c)-(e) one-bit TR with a threshold of 0.2, indicated by the dashed black lines, (f)-(h) clipping TR with a threshold of 0.2, (i)-(k) decay compensation TR with a threshold of 0.06.
Clipping TR, a fairly new technique, is very similar to one-bit TR apart from one key difference. A threshold, $T_{CP}$, is applied to the impulse response, just as with one-bit TR, and if $|r(-t_i)| \geq T_{CP}$, then $r(-t_i) \equiv \text{sign}(r(-t_i)) \cdot T_{CP}$. However, any signal below the threshold is not set equal to zero as with one-bit TR processing and instead is unmodified (see Figs. 3(f)-(g) where threshold is 0.2). When this resulting signal is normalized, any “clipped” signal is set to one and all of the signal that was below the threshold is amplified relative to the original normalized impulse response (see Fig. 3(h)). Like one-bit TR, clipping TR amplifies later reflections, but it also amplifies all low-level signal in the recorded impulse response, potentially amplifying background noise.

Decay compensation TR attempts to compensate for the exponential decay of the impulse response. As explained by Willardson et al., the envelope of the RIR is obtained through a Hilbert transform operation, after which the envelope is smoothed through the use of a moving average filter (see Fig. 3(i)). The envelope is inverted and normalized and then multiplied by the original, normalized RIR, point by point, creating a signal with approximately the same amplitude over all time (see Fig. 3(j)). Because this can amplify unwanted noise, a threshold is applied with respect to the decay curve such that if the instantaneous value of the decay curve is below the threshold, the modified signal retains the values of the original, normalized, RIR. An example signal after the decay compensation TR processing is shown in Fig. 3(k) with an applied threshold of 0.06.
IV. FOCAL SIGNAL ANALYSIS METRICS

Four primary metrics are used to quantify the relative merits of the focal signals generated by each of these impulse response modification techniques, three of which were introduced by Denison and Anderson.38 The processing methods of deconvolution, one-bit, clipping, and decay compensation each result in changing more than just peak focal amplitude and can often result in significant drawbacks along with their benefits. By applying quantitative measures to the focal signal, some of these drawbacks are identified, especially as related to adjustments in the threshold value used in each case. The first metric is the value of the peak amplitude in the time domain waveform at the location of the focus (the focal signal), called the peak focal amplitude, \( A_p \). The second metric, called temporal quality, \( \xi_t \), is a ratio of the instantaneous energy contained in \( A_p \) to the average energy in the entire focal signal, \( A(x_0, y_0, t) \), of number of time samples \( N \), at the focal location \( (x_0, y_0) \),

\[
\xi_t = \frac{\sqrt{\frac{[A_p]^2}{\frac{1}{N} \sum_{n=1}^{N} [A(x_0, y_0, n)]^2}}}.
\]  

A square root operation is used to express the ratio of these energy quantities as a ratio of amplitudes. While variations in the result for Eq. (2) can be obtained by using different time windows of the signal, for this study, the entire 51.2 ms signal was used. \( \xi_t \) illuminates characteristics of the focal signal otherwise only gleaned from a visual examination of time waveforms, such as the amplitude of the side lobes compared to \( A_p \).

Spatial quality, \( \xi_s \), the third metric, defines a ratio of the energy in the peak focal amplitude, \( A_p \), which occurs at the focal location, to the average energy of the spatial locations that surround it at the time of the focus, \( t_0 \),
\[ \xi_s = \frac{1}{\sqrt{M_x M_y \sum_{m_x=1}^{M_x} \sum_{m_y=1}^{M_y} [A(m_x, m_y, t_0)]^2}} \]  

where \( M_x \) and \( M_y \) are the number of spatial locations sampled in the \( x \) and \( y \) directions, respectively. The velocity at each point, \( A(m_x, m_y, t) \), is measured as the TR process is repeated while the SLDV records the velocity at \( M_x \times M_y \) spatial points both at and surrounding the focal location. At \( t_0 \), \( \xi_s \) represents how significant the peak amplitude is to the rest of the amplitude over the entire scan area. Given in conjunction with \( \xi_s \) are values for the full-width-half-maximum (FWHM) values for the spatial extent of the focusing. The FWHM is determined from two cross sectional plots of the instantaneous squared velocity along the \( x \) and \( y \) axes in the spatial map of the focusing to determine the full width of the focus at half the maximum amplitude.

The fourth metric examines the harmonic content of the spectrum of the focal signal (the focal spectrum) by quantifying a ratio of the energy contained in the fundamental frequency bandwidth (75-125 kHz), to the second (150-250 kHz) or third (225-375 kHz) harmonic frequency bandwidth. Because the chirp of the forward propagation step has a finite bandwidth, the frequency content of the focal spectrum for traditional TR should be limited to the fundamental bandwidth. Any second or third harmonics of the fundamental bandwidth that occur can only be a result of nonlinearity in the system, whether that is the physical system or any nonlinear signal processing. Mathematically, the fundamental-to-second harmonic ratio, \( R_{12} \), is

\[ R_{12} = 10 \log_{10} \left( \frac{\frac{1}{N_1} \sum_{f_0}^f |F|^2}{\frac{1}{N_2} \sum_{2f_0}^{2f_1} |F|^2} \right) \]  

The absolute value of the square of the focal spectrum, \( |F|^2 \), is summed across the values between \( f_0 = 75 \) kHz and \( f_1 = 125 \) kHz, the fundamental bandwidth, then scaled by the number
of points within that bandwidth, \( N_1 \). This quantity is divided by a similar term wherein \( |F|^2 \) has been summed across the values between \( 2f_0 \) and \( 2f_1 \), the second harmonic, and divided by \( N_2 \), the number of frequency points in the second harmonic. The fundamental-to-third harmonic ratio, \( R_{13} \), is defined similarly,

\[
R_{13} = 10 \log_{10} \left( \frac{\frac{1}{N_1} \sum_{f_0}^{f_1} |F|^2}{\frac{1}{N_3} \sum_{3f_0}^{3f_1} |F|^2} \right). \tag{5}
\]

V. RESULTS

In examining the focal signals, many of the benefits and drawbacks of these impulse response modification techniques are made manifest. Figure 4 shows five example focal signals. Each were measured at the same focal location using the same source chirp signal and thus start out with the same impulse response signal, but this impulse response was then processed with the five different signal processing modification techniques described in Section III. Figure 4(a) shows the focal signal generated using an unmodified impulse response, or traditional TR, where an impulse response is only flipped in time and broadcast to generate a focal signal. This focal signal has the expected symmetrical side lobes with a \( A_p = 10 \text{ mm/s} \) and \( \xi_t = 34.1 \), and is the baseline against which all of the other focal signals are compared. The focal signal shown in Fig. 4(b) uses deconvolution TR and one may observe that, relative to traditional TR, the energy in the side lobes are reduced in the focal signal (shown in Fig. 4(b)) resulting in a signal that more closely approximates a delta function. This is confirmed by the \( \xi_t \) which equals 60 for deconvolution TR, however, this benefit is obtained at the expense of a reduction in \( A_p \) to 5mm/s, a factor of two relative to traditional TR. A one-bit TR focal signal is shown in Fig. 4(c) with a \( A_p = 30 \text{ mm/s} \). This focal signal employed a threshold value of 0.02 to amplify the impulse response, which
increases the $A_p$ but also dramatically increases the amplitude of the side lobes prior to the focus, resulting in a non-symmetrical focal signal with $\xi_t = 24.2$. Even more non-symmetric side lobe amplitudes are evident in the clipping TR focal signal in Fig. 4(d) where $\xi_t = 22.2$. This focal signal also employs a threshold of 0.02 but is able to reach a $A_p = 32$ mm/s. The focal signal displayed in Fig. 4(e) is generated with decay compensation TR also at a threshold of 0.02. The $A_p = 27$ mm/s here is not quite as high as that shown in Figure 4(c) and (d), but the heavily asymmetric side lobes are just as evident, as indicated by $\xi_t = 22.5$.

FIG. 4. (color online) Measured focus signals using (a) traditional, (b) deconvolution, (c) one-bit, (d) clipping, and (e) decay compensation TR. One-bit, clipping, and decay compensation TR all use a threshold value of 0.02.
**A. Peak Focal Amplitude**

As explained previously, the threshold used in the modification techniques of one-bit, clipping, and decay compensation TR can be defined as any number between zero and one, where a lower number ultimately boosts low amplitude arrivals later in the impulse response relative to the higher amplitude arrivals earlier in the impulse response. This sends more energy overall into the medium, upon normalization of the reversed signal, which is then broadcast in the backward propagation step. Figure 5 reports the $A_p$ measured from all five processing techniques versus the threshold applied. The $A_p$ of traditional TR and deconvolution TR are plotted with a threshold value of one because they do not use a threshold in their processing but are worth comparing to. At the lowest thresholds shown, between $10^{-4}$ and $10^{-3}$, the $A_p$ of one-bit, clipping, and decay compensation TR all plateau at around 29 mm/s. At these thresholds, all of the coherent signal has been amplified during the impulse response processing and thus no further gains in $A_p$ are possible. Though not shown, focal signals were actually obtained with thresholds as low as $10^{-12}$ and it was found that $A_p$ did not increase beyond the 28-30 mm/s region. In the vicinity of a threshold value of 0.01, one-bit and clipping TR provide a maximal $A_p$. These maxima are likely a balance between amplifying late arrivals in the impulse response and amplifying background noise in the impulse response. Any noise that is amplified generates destructive interference while any amplified late reflections will constructively interfere in the TR focusing. On the contrary, the $A_p$ of decay compensation TR is optimal only at the lowest threshold values and converges to traditional TR at a threshold of one. One-bit and clipping TR are maximized at thresholds of 0.007 and 0.02 respectively with clipping TR reaching the highest overall peak focal amplitude of 31 mm/s. Both methods achieve lower $A_p$ as the threshold is increased with clipping TR being
equivalent to traditional TR at the limiting value of one and the $A_p$ for one-bit TR going to zero. Clipping TR merges with traditional TR and one-bit TR does not at a threshold of one because these techniques treat the signal below the threshold differently. One-bit TR zeros out the signal below the threshold while clipping TR leaves it intact meaning that a threshold of one would leave one-bit TR with an impulse response of mostly zeros with a single sample value set to one. The resulting TR focal signal is not a focus at all but merely a low amplitude impulse response. Clipping TR would return a traditional focal signal for a threshold of one. Decay compensation TR merges with traditional TR at a threshold of one for reasons similar to clipping TR.

FIG. 5. (color online) Peak focal amplitude, $A_p$, vs threshold applied obtained from time reversal (TR) focal signals with various TR processing techniques applied. Traditional TR and deconvolution TR do not use a threshold and so are plotted at a threshold of one.

B. Temporal Quality

$x_t$ was calculated for the focal signals obtained with a range of thresholds and is a second instructive way to study the impact of threshold for each method. The curves displayed in Fig. 6
show an overall increase in $\xi_t$ with an increasing threshold, reaching an approximate maximum at a threshold value of one when the curves merge with traditional TR. This indicates that, aside from deconvolution TR, traditional TR has the lowest amplitude side lobes and therefore the cleanest focal signal. The application of a threshold for one-bit, clipping, and decay compensation TR techniques results in an increase in the amplitude of side lobes in exchange for a gain in $A_p$. The notable exception is one-bit TR, which never collapses with traditional TR, as described in the previous paragraph, but instead drops sharply in $\xi_t$ over thresholds from 0.3 to 1. The overarching trade-off presented by the threshold analysis is that a lower threshold results in higher $A_p$ with a decrease in $\xi_t$. A high threshold results in a high $\xi_t$ but lower $A_p$. The application of the TR processing is then what should determine whether maximal $A_p$ or maximal $\xi_t$ is more important.

For crack detection in NDE, high $A_p$, whatever the processing used to obtain it, is assumed to be ideal for the excitation of nonlinear vibrations of a crack. While high $\xi_t$ produces very clean signals, which is important for communications applications for example, the accompanying low $A_p$ likely makes it unsuitable for crack detection, and thus it will not be further explored. With this in mind the optimal threshold value for one-bit, clipping, and decay compensation TR techniques is suggested to be 0.02 to yield a high $A_p$ while maintaining a reasonably high $\xi_t$.

C. Spatial Quality

$\xi_s$ was calculated according to Eq. (3) using the spatial scans collected for each of the five signal processing techniques. Table 1 shows the results of this analysis where one-bit, clipping, and decay compensation TR are generated with thresholds of 0.02. In the first data column, $\xi_s$ for decay compensation TR gives the highest value of 4.6, indicating that decay compensation has the most energy in its peak focal value relative to the energy in the field around it. Each of the
modification techniques yields a higher $\xi_s$ than the value obtained for traditional TR. It is interesting that one-bit TR, clipping TR, and decay compensation TR all yield higher $\xi_s$ values since the side lobes for each of these techniques are higher than obtained with traditional TR as observed in Fig. 6.

FIG. 6. (color online) Temporal quality, $\xi_t$, vs threshold applied obtained from time reversal (TR) focal signals with various TR processing techniques applied. Traditional TR and deconvolution TR are plotted at a threshold value of one.

The FWHM is smaller for all techniques relative to traditional TR. This is not surprising for deconvolution TR since the purpose of this technique is to temporally and spatially compress the focus. The FWHMs for one-bit, clipping, and decay compensation TR are smaller than traditional TR, a somewhat surprising result, but helpful in this case since it shows that they do not increase the spatial extent of the focus. A larger focal size could decrease the resolution with which cracks can be detected, making crack detection less reliable overall. However, since this is not the
case for any of the modification techniques shown here, the benefits to crack detection of a
spatially compressed TR focus remain intact.

TABLE 1. Spatial quality and full-width-half-max (FWHM) of the spatial scans taken of a focal
signal for each time reversal (TR) signal processing technique. A threshold of 0.02 was used for
one-bit, clipping, and decay compensation TR techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>$\xi_s$</th>
<th>FWHM (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional TR</td>
<td>3.5</td>
<td>13.6</td>
</tr>
<tr>
<td>Deconvolution TR</td>
<td>3.9</td>
<td>12.6</td>
</tr>
<tr>
<td>One-bit TR</td>
<td>4.4</td>
<td>12.3</td>
</tr>
<tr>
<td>Clipping TR</td>
<td>4.3</td>
<td>12.8</td>
</tr>
<tr>
<td>Decay Compensation TR</td>
<td>4.6</td>
<td>12.5</td>
</tr>
</tbody>
</table>

D. Harmonic Generation

Because one-bit, clipping, and decay compensation TR utilize nonlinear processing of the
RIR, an examination of the spectral content of the focal signals is vital. Nonlinear frequency
content generated by the impulse response modification techniques effectively raises the noise
floor in harmonic frequency bands, thereby decreasing the ability to detect harmonic generation in
a focal signal. Focal spectra of the focal signals measured using one-bit, clipping, and decay
compensation TR, are shown in Figs. 7(b)-(d), respectively. The threshold used for all three
methods is 0.02, the same as the focal signals shown in Fig. 4, and is the optimal threshold value
as determined in the previous sections. The focal spectrum created using traditional TR is helpful
for comparison and is given in Fig. 7(a). In each plot in Fig. 7, the fundamental bandwidth is defined as the frequency content between the two solid vertical lines (75-125 kHz), the second harmonic bandwidth is between the two dashed vertical lines (150-250 kHz), and the third harmonic bandwidth is between the two dash-dot vertical lines (225-375 kHz). With these bandwidths defined, the amplitudes in each bandwidth may be compared. The fundamental bandwidth amplitude is clearly the lowest in traditional TR and the highest for clipping TR, which is expected given their peak focal amplitudes. For the second and third harmonics, this is not true. Traditional TR appears to contain only uncorrelated background noise in the harmonic bandwidths, increasing somewhat with frequency above 300 kHz. Both clipping and one-bit TR spectra exhibit a marked increase in harmonic amplitudes, especially for the third harmonic. In fact, both clipping and one-bit TR exhibit increases in the fifth harmonic amplitudes as well. Decay compensation TR does exhibit an increase in harmonic content, but this introduction of higher frequency content decreases as frequency increases (until 425 kHz) and the levels of the harmonic amplitudes are at least half as high as in clipping and one-bit TR. All three techniques are nonlinear processes but clearly the other two are more nonlinear than decay compensation TR.

On closer examination of the higher frequency spectra of clipping and one-bit TR, the marked increases in harmonic amplitudes centered about 300 and 500 kHz represent odd harmonics of the fundamental peak centered about 100 kHz. This is because the two techniques essentially create square waves, which have prominent odd harmonics. Decay compensation TR does not alter the waveform structure as dramatically; so, while decay compensation TR does generate some increase in harmonic amplitudes, it is not nearly as prominent as the increases introduced by clipping and one-bit TR.
FIG. 7. (color online) The focal spectra measured with (a) traditional time reversal (TR), (b) one-bit TR, (c) clipping TR, (d) decay compensation TR. (b)-(d) use a threshold of 0.02 for the impulse response modification. The region between the solid vertical lines is the fundamental bandwidth (75-125 kHz). The region between the dashed lines is the second harmonic (150-250 kHz), and the region between the dash-dot lines is the third harmonic (225-375 kHz).

To better quantify the harmonic content, ratios between the first harmonic and the second or third harmonic bandwidths can be calculated using Eqs. (4) and (5). The results of these calculations are shown in Table 2. The best case scenario for a harmonic ratio is traditional TR, which only has background noise at the harmonic frequencies and so has the largest ratios of $R_{12} = 37$ dB and $R_{13} = 34$ dB. The next best is decay compensation TR, which has a lower $R_{12} = 35$ dB, but an equal $R_{13} = 34$ dB. It is clear in Fig. 7 that the amplitude of the third harmonic is higher for decay compensation TR than for traditional TR, but the fundamental amplitude also is markedly higher for decay compensation TR than for traditional TR. The ratios for clipping and
one-bit TR are lower, especially for $R_{13}$, for the reasons identified in the previous paragraph. It should be remembered that when a crack vibrates it does so nonlinearly and thus a higher amplitude excitation raises the harmonic frequency amplitudes by more than any increase in the fundamental frequency amplitude. Thus, while these modification techniques have lower fundamental to higher harmonic amplitude ratios, they each should be able to induce a larger nonlinear response of a crack.

TABLE 2. Harmonic ratios: the ratio of the energy in the fundamental bandwidth to the energy in a higher harmonic, shown below for the second harmonic, $R_{12}$, and the third harmonic, $R_{13}$ for each of the amplitude-increasing modification techniques and traditional time reversal (TR).

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<th>$R_{12}$ (dB)</th>
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<td>24</td>
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<td>26</td>
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<tr>
<td>Decay Compensation TR</td>
<td>35</td>
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VI. NONLINEAR DETECTION OF SCC USING DECAY COMPENSATION TR

Because decay compensation TR has shown to provide higher $A_P$, without a significant decrease in $R_{12}$ and $R_{13}$, a preliminary study was conducted for nonlinear TR crack detection using decay compensation TR as the means of excitation to detect stress corrosion cracking (SCC). SCC is known to develop in steel in the Heat-Affected-Zone surrounding welds that are exposed to harsh environments. To obtain a sample with SCC, a 304L steel rod, 12.7 cm (5 in) in length and
1.59 cm (5/8 in) in diameter, is cut in half and welded back together. The sample is then exposed to a 42% magnesium chloride bath at a temperature of 80°C for 16 days, following recommendations of Jackson et al. The creation of these damaged samples was described by Hogg et al. and Young et al. After exposure the rod is epoxied to the top of the disk used in the previous study and to the bottom of the disk are epoxied eight piezoelectric transducers (APC, material type 850) with diameter 19 mm and thickness 12 mm. The piezoelectric transducers are connected to two 4-channel, 50x gain, Tabor 9400 amplifiers that in turn are connected to a National Instruments (Austin, Texas) PXI-7852R 8-channel generator card. A SLDV, externally controlled by custom LabVIEW-based software, is directed to scan 200 points along a 50 mm length of the rod (0.25 mm spacing between scan points), extending roughly 20 mm to either side of the edge of the weld. For each scan point, each of the eight generation channels, in turn, emits a 2 V, 75-125 kHz chirp signal and each of the chirp responses are measured at the current scan point with the SLDV. Eight RIRs are calculated, using either traditional TR or decay compensation TR, and are simultaneously emitted from the piezoelectric transducers at 0.25 V and then again at 1.5 V. A TR focus of energy is generated by each transducer and the simultaneous emission of all 8 transducers ensures that these foci superpose at the scan location. The SLDV has a sensitivity of 25 mm/s/V and the signal is acquired with a National Instruments PXIe-5122 Digitizer with 14-bit resolution. In a previous study Young et al. used this sample and others like it to determine that the amplitude of the second harmonic generally increased with longer exposure to the magnesium chloride bath as described previously due to the increasing amount of SCC in the rods.

At each scan location, it is possible to calculate the nonlinearity present in the focal signal recorded at that location by obtaining the cumulative amplitude of the second harmonic, $E_2$, where
\[ E_2 = \sum_{150kHz}^{250kHz} |F|^2. \]  

(6)

\( E_2 \) is plotted versus the location of the scan point in E. 8(a)-(b) to determine where along the rod nonlinearity from the second harmonic was highest and therefore SCC is more likely to exist. The detection ability of decay compensation TR can be directly compared to that of traditional TR, point by point, in Fig. 8 with \( E_2 \) versus distance normalized by the peak value detected with each technique. Because the foci measured using decay compensation TR are an average of two times higher than those measured using traditional TR, the second harmonic of decay compensation TR is also higher at every scan point and thus normalization better compares the peaks in nonlinearity to the supposed background nonlinearity levels at locations where SCC is not expected.

Given the propensity to damage formation in the heat-affected-zone, second harmonic nonlinearity is expected to increase in the assumed Heat-Affected-Zone regions spanning 9-19 mm and 30-40 mm on either side of the weld. Two vertical dashed lines at 19 mm and 30 mm give the approximate location of the outer edge of the weld, meaning the material between 19-30 mm is comprised of the weld itself. In Fig. 8(a), where a 0.25 V excitation was used, the most notable distinction between the two techniques is that traditional TR presents higher values of normalized nonlinearity than decay compensation TR at various locations. Both techniques detect a strong feature at 34 mm in the expected region just outside of the weld. The peak at 34 mm was chosen as the normalization constant because the amplitude was consistently high across several scan points. At 8 mm a large peak is evident in the traditional TR data nearly of the same amplitude as the feature at 34 mm. The decay compensation TR data on the other hand does not exhibit as large an amplitude feature at 8 mm as at 34 mm. The seemingly random peaks in the traditional TR data at 2, 12, 24, 27, 38, 39, 47, 48, and 50 mm are at individual scan points, calling these features into question. The decay compensation TR data is smoother from scan point to scan point. Other than
the main peak at 34 mm and the small one at 8 mm, the nonlinearity in the decay compensation TR data oscillates at low levels indicative of consistent background nonlinearity.

FIG. 8. (color online) Normalized nonlinearity contained in the second harmonic of a focal signal, shown as $E_2$ on the vertical axis, generated at each of 200 scan locations along a rod with stress corrosion cracking. Traditional time reversal (TR) (black) and decay compensation TR (dotted) were used to excite TR foci at each location. Figure 8(a) shows the results when the focal signals were excited with an amplitude of 0.25 V. Figure 8(b) shows the results at an excitation amplitude of 1.5 V. While ultimately unknown, stress corrosion cracking is likely to occur in the region just outside the weld on the rod, called the Heat-Affected-Zone.

Figure 8(b) shows the same scan taken at an excitation amplitude of 1.5 V. The decay compensation TR data looks essentially the same, though a bit more smooth, suggesting that the
amplitude of the 0.25 V measurement was sufficiently above the noise floor to result in reliable measurements. The data of traditional TR in Fig. 8(b) is drastically different, with all of the seemingly random peaks removed and even the gradual rises at 8 mm and 27 mm significantly reduced. With the increase in excitation amplitude, the traditional TR result nearly merges with the decay compensation TR measurement. This indicates that decay compensation TR is not only able to measure nonlinearity from SCC as well as traditional TR, but is also more reliable at lower excitation levels where traditional TR struggles. Additionally, false detections of features at 8 mm and 27 mm in the traditional TR data are not present at either excitation level for decay compensation TR.

VII. CONCLUSION

Time reversal (TR) focusing used for the purpose of exciting nonlinearity in cracks has the potential to suffer from a low signal to noise ratio (SNR) and therefore false detections if only traditional TR techniques are utilized. Modifications to the reversed impulse response, wherein later reflections are amplified relative to early reflections, ultimately increases the peak focal amplitude, but often at the expense of lowering the temporal quality of the focal signal, and increasing higher-order harmonics, a problem for nonlinear crack detection that relies on higher-order harmonics to sense cracks. Four techniques were studied relative to traditional TR, deconvolution, one-bit, clipping, and decay compensation TR. One-bit, clipping, and decay compensation TR were able to realize focal amplitudes 3 times higher than traditional TR. Deconvolution TR had a temporal quality much higher than any other technique, but with a focal amplitude that was much lower. Only decay compensation TR significantly increased peak focal amplitude without a drastic increase in higher harmonic content as well. In addition, spatial focus
quality and the width of the focusing was found to be slightly better for the 4 modification
techniques than for traditional TR. In the study of TR optimization in a reverberation chamber,
Willardson et al. found results similar to these, but with clipping TR able to reach amplitudes over
4 times higher than traditional TR at a threshold value of 0.03.

Decay compensation TR was utilized to locate regions of high nonlinearity on a rod with
stress corrosion cracking. These were then compared to results from the same test conducted using
traditional TR. It was determined that, because of decay compensation TR’s higher SNR in its
focal signals, it was able to more cleanly detect nonlinearity compared to traditional TR. In
addition, when the experiment was repeated at higher excitation amplitudes, the random spikes in
nonlinearity and a couple of false detections measured at the low excitation level with traditional
TR disappeared and the data tended to converge to the data found with decay compensation TR.

ACKNOWLEDGEMENTS

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TABLE 1. Spatial quality and full-width-half-max (FWHM) of the spatial scans taken of a focal signal for each time reversal (TR) signal processing technique. A threshold of 0.02 was used for one-bit, clipping, and decay compensation TR techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>$\xi_s$ (mm)</th>
<th>FWHM (mm)</th>
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<tbody>
<tr>
<td>Traditional TR</td>
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<td>13.6</td>
</tr>
<tr>
<td>Deconvolution TR</td>
<td>3.9</td>
<td>12.6</td>
</tr>
<tr>
<td>One-bit TR</td>
<td>4.4</td>
<td>12.3</td>
</tr>
<tr>
<td>Clipping TR</td>
<td>4.3</td>
<td>12.8</td>
</tr>
<tr>
<td>Decay Compensation TR</td>
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TABLE 2. Harmonic ratios: the ratio of the energy in the fundamental bandwidth to the energy in a higher harmonic, shown below for the second harmonic, $R_{12}$, and the third harmonic, $R_{13}$ for each of the amplitude-increasing modification techniques and traditional time reversal (TR).

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</table>
FIG. 1. Example signals used in the time reversal process. Except for (e), the amplitudes are normalized and are in arbitrary units. (a) Source chirp (with frequencies altered for visualization), (b) chirp response, (c) impulse response, (d) reversed impulse response, (e) focal signal.

FIG. 2. (color online) Experimental setup with scanning laser Doppler vibrometer (SLDV) pointed at a steel disk. The steel disk has a piezoelectric transducer (PZT) epoxied to the bottom.

FIG. 3. (color online) Impulse response modification techniques with each starting with a traditional RIR, (a)-(b) deconvolution TR, (c)-(e) one-bit TR with a threshold of 0.2, indicated by the dashed black lines, (f)-(h) clipping TR with a threshold of 0.2, (i)-(k) decay compensation TR with a threshold of 0.06.

FIG. 4. (color online) Measured focus signals using (a) traditional, (b) deconvolution, (c) one-bit, (d) clipping, and (e) decay compensation TR. One-bit, clipping, and decay compensation TR all use a threshold value of 0.02.

FIG. 5. (color online) Peak focal amplitude, $A_p$, vs threshold applied obtained from time reversal (TR) focal signals with various TR processing techniques applied. Traditional TR and deconvolution TR do not use a threshold and so are plotted at a threshold of one.

FIG. 6. (color online) Temporal quality, $\xi_t$, vs threshold applied obtained from time reversal (TR) focal signals with various TR processing techniques applied. Traditional TR and deconvolution TR are plotted at a threshold value of one.
FIG. 7. (color online) The focal spectra measured with (a) traditional time reversal (TR), (b) one-bit TR, (c) clipping TR, (d) decay compensation TR. (b)-(d) use a threshold of 0.02 for the impulse response modification. The region between the solid vertical lines is the fundamental bandwidth (75-125 kHz). The region between the dashed lines is the second harmonic (150-250 kHz), and the region between the dash-dot lines is the third harmonic (225-375 kHz).

FIG. 8. (color online) Normalized nonlinearity contained in the second harmonic of a focal signal, shown as $E_2$ on the vertical axis, generated at each of 200 scan locations along a rod with stress corrosion cracking. Traditional time reversal (TR) (black) and decay compensation TR (dotted) were used to excite TR foci at each location. Figure 8(a) shows the results when the focal signals were excited with an amplitude of 0.25 V. Figure 8(b) shows the results at an excitation amplitude of 1.5 V. While ultimately unknown, stress corrosion cracking is likely to occur in the region just outside the weld on the rod, called the Heat-Affected-Zone.
Detecting and Imaging Stress Corrosion Cracking in Stainless Steel, with Application to Inspecting Storage Canisters for Spent Nuclear Fuel

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Abstract

One of the primary concerns with the long-term performance of storage systems for spent nuclear fuel (SNF) is the potential for corrosion initiation due to deliquescence of salts deposited as aerosols on the surface of the canister, which is typically made of austenitic stainless steel. In regions of high residual weld stresses, this may lead to localized stress-corrosion cracking (SCC). The ability to detect and image SCC at an early stage (long before the cracks are susceptible to propagate through the thickness of the canister wall and leaks of radioactive material may occur) is essential to the performance evaluation and licensing process of the storage systems. In this paper, we explore a number of nondestructive testing techniques to detect and image SCC in austenitic stainless steel. Our attention is focused on a small rectangular sample of 1×2 in² with two cracks of mm-scale sizes. The techniques explored in this paper include nonlinear resonant ultrasound spectroscopy (NRUS) for detection, Linear Elastodynamic Gradient Imaging Technique (LEGIT), ultrasonic C-scan, vibrothermography, and synchrotron X-ray diffraction for
imaging. Results obtained from these techniques are compared. Cracks of mm-scale sizes can be detected and imaged with all the techniques explored in this study.

1. Introduction
Currently Spent Nuclear Fuel (SNF) is stored in two types of environmental storage conditions; 1) submerged in water in pools at reactor facilities, and 2) in dry storage at Independent Spent Fuel Storage Installations (ISFSIs), adjacent to reactor facilities. Generally after a few years of cooling time, SNF is removed from the water pool and transferred to helium-filled stainless steel canisters and stored in a passively ventilated concrete overpack, which acts as a dry storage systems. As a result of several recent decisions, such as not pursuing Yucca Mountain as a long-term geologic repository storage facility for SNF and the cancellation of the construction of a reprocessing facility in the 1980s due to proliferation risks, interim dry storage facilities for long-term storage are vital for the immediate future of nuclear energy technology. One of the primary concerns with respect to the long-term performance of the storage casks is the potential for corrosion initiation due to deliquescence of salts deposited on the canister surface as aerosols. In regions of high residual weld stresses, this may lead to localized stress corrosion cracking (SCC). Dust and aerosols in the air being drawn through ventilation openings in the concrete overpack may be deposited on the stainless steel canister outer surfaces. Under these conditions, localized corrosion may occur. Chloride-induced stress corrosion cracking (CISCC) of welded heat affected zones (HAZ) is of special concern, as it is a well-documented mode of attack for austenitic stainless steels (including 304H/L and 316L) in marine environments [1], and many ISFSI sites are located in coastal areas. Recent canister inspections [2,3] have shown that chloride salts are present on the surface of in-service canisters in near-marine sites.

For a number of safety reasons, it is strongly preferred to leave the canister inside the concrete overpack once installed there. This makes the inspection of canister surfaces very challenging, mainly because of the harsh environment and space constraints. The inspection system should be designed to sustain high temperatures (typically 205°C upon loading the canister into the overpack down to less than 150°C after 30 years) and gamma radiation (in the range of $10^3$ to $10^5$ rad/h) [4]. The space constraints include restricted access through the narrow ventilation system and narrow rectangular channels between the overpack and the canister. On the HI-STORM 100 model cask
(Holtec International, Turtle Creek, PA, USA), these channels have dimensions of 50 mm by 150 mm [4]. All the welds and associated HAZs cannot be visible or accessible from all the channels, thus leaving some blind spots that cannot be inspected with visual techniques. Some recent work from the group of Lissenden at Pennsylvania State University has shown the possibility to access and inspect this tight space with robots instrumented with EMAT acoustic sensors [5,6]. The detection technique they used is based on the acoustic echoes generated by defects along the propagation path of the wave. They demonstrated their approach on a sample that had a notch in the HAZ to simulate the presence of a crack. The notch could be detected but so could the reflection from the back wall, the weld, and other reflectors. Similar limitations would be encountered with any technique based on linear acoustics or linear wave propagation, including C-scans, eddy currents, or angle-beam ultrasound. Furthermore, in the early stage of damage or under certain stress conditions, the crack may be present but not necessarily open, in which case no reflection of the incident acoustic wave would be produced, thus possibly making the crack invisible to these techniques.

This paper focuses on a number of techniques based on acoustics and/or optics that adapted to the detection and imaging of cracks at an early stage of damage. To this end, a sample with small cracks (less than 2 mm in length) is used throughout the study. Some of the crack detection techniques, such as ultrasonic C-scan, are well established in the field [7], while others, such as Linear Elastodynamic Gradient Imaging Technique (LEGIT), have been developed in-house. Each crack-detection technique is introduced briefly here, since additional background information is provided in the individual sections for each technique. Last, detailed 3D images of the cracks are created using synchrotron X-ray diffraction, which is used only as a reference here without any objective of field deployment.

The first technique discussed is ultrasonic C-scan, which relies on linear ultrasonics. When an ultrasonic wave is propagated in the vicinity of an open crack, the crack creates an echo whose amplitude can be measured to create an image of the crack [8]. Linear Elastodynamic Gradient Imaging Technique (LEGIT), was developed to quickly image cracks using a laser vibrometer. For this method, a crack is excited via ultrasonic waves and imaged by taking the gradient of the dynamic response in the frequency domain. Nonlinear Resonant Ultrasound Spectroscopy (NRUS) is another ultrasonic technique used in this study to detect (as opposed to image) the presence of a crack. NRUS was first developed to measure the nonclassical, hysteretic component of material
nonlinearity by tracking the change in resonance frequency with increasing strain amplitude [9,10]. The next technique discussed, vibrothermography, also utilizes ultrasonic waves to excite a crack, however, the imaging methodology is based on heat generation [11]. As a crack is excited, the clapping of the crack faces generates heat, which in turn can be imaged with an Infrared (IR) camera [12]. Finally, measurements using synchrotron X-ray tomography are presented. Micro X-ray tomography is a non-destructive technique that utilizes the differences in phase contrast between the crack and the material [13]. The sample is rotated 360° and a series of 2-D X-ray projections are taken and reconstructed to produce a 3-D representation of the crack.

2. Sample Description and Optical Imaging of the Cracks

The multiple crevice assembly (MCA) method described in ASTM G4829 and previous studies [14-16] was adopted to study the crevice corrosion and stress corrosion cracking behavior of type 304-09A stainless steel. The sample used in this study is shown in Fig. 1. The 304-09A compression washer specimen (50×25×1.4mm) was fabricated from a wrought plate, with a through-hole geometry (6.8-mm diameter) in the center of the specimen (Fig. 2b). The test surfaces of the MCA specimen were ground with 600-grit, wet silicon carbide (SiC) paper and ultrasonically cleaned with methanol for a period of 10 minutes before the test. A mixture of NaCl and KCl (50:50) salts were deposited on the specimen surface via an airbrush with a methanol carrier (6 passes). The deposition density was measured as 99.1 µg/cm² with a quartz crystal microbalance (QCM) during deposition. Once deposited, the polytetrafluoroethylene (PTFE) tape covered ceramic crevice former was used to form the crevices. Each crevice former had 12 crevice contacts and the area of each crevice contact was 0.06 cm². The PTFE tape was standard military-grade thread sealant tape with an initial thickness of 76 µm. The crevice former is shown in Fig. 2a. The specimen and two crevice formers were assembled together with two grade 2 titanium bolts, nuts and washers, with an applied torque of 7.91 Nm (70 in-lbs). The titanium bolts, nuts and washers were electrically isolated from the specimen with the PTFE tape. Fig. 2b shows the MCA assembly with two crevice formers. The sample was then exposed to a 105 °C environment with a dew point of 95 °C for 100 days.
Optical observation of the crack on sample surface only show part of the whole crack along the radial direction of the hole (Fig. 3). The surface crack start to appear on the specimen surface at a distance of 463 µm away from the edge of the hole. Under optical microscope, the crack also appear at the middle region of the edge of the hole. Several pitting sites are found along the crack path, and more pits are found at other regions on the specimen surface. Large corrosion areas are found at the crevice contact regions. The corrosion area at the top left in Fig. 3 is a small part of the crevice contact region.
Fig. 3. Optical image of the crack and pits on sample surface. The schematic drawing is used for better understanding of the location of surface crack. Dash oval indicates some pitting sites, solid rectangle indicates surface crack and solid oval shows the crack in the middle region of the edge of the hole.

An enlarged view of the surface crack with a total length of 830 µm is shown in Fig. 4. Pitting sites are indicated with arrows. There are several pitting sites along the crack path. Fig. 4a shows two pits that are connected by the surface crack on the lower left side. Corrosion products are found around these pits. Two large crack deviation regions (Figs. 4b and c) and several small crack jumps (Fig. 5) are also found along the crack path; cracks in these regions are disconnected on the specimen surface under optical observation. The crack appears to originate from surface locations (pitting sites).
Fig. 4. Enlarged view of the surface crack, pitting sites and crack deviation regions. (a) Two large pitting sites along the crack path and corrosion products around the pits; (b) and (c) two large crack deviation regions along crack path.

Fig. 5. (a)-(d) Small crack jumps along the crack path on sample surface.
3. Ultrasonic C-Scan

Ultrasonic testing that employs linear elastic-wave propagation in a sample has been widely used for the inspection of optically nontransparent materials such as metallic samples. Frequencies on the order of MHz are typically selected in contact testing, where the ultrasonic piezoelectric transducer are contacted to the specimen through liquid coupling gel [7,8,17]. Because this is a linear technique based on the scattering of the elastic waves by the defects, the wavelength used for testing should similar in size or smaller than the defect to be imaged. This requirement typically results in operating frequencies ranging from MHz to GHz for water (or other coupling liquid) immersion testing [18-23]. Note that C-scans cannot be conducted through air (with air-coupled transducers) because of the large attenuation and impedance mismatch between air and the sample at these frequencies. In this method, a sample is immersed in a tank with a liquid that is mainly water. In most cases, a geometrically focused transducer is employed to enhance both resolution and sensitivity. Ultrasound emitted from a focused transducer propagates in water to a sample and reaches the top surface of the specimen. When the focused transducer is placed so that a focal point matches just on the top surface of the specimen, the maximum reflection is obtained on the surface. As the focused transducer is moved close to the sample, the focal point is newly created within the sample. Due to the refraction of ultrasound at the top surface of the sample, the distance between the focused transducer and the focal point is shorter than the original focal length determined by the geometry of the focused transducer. The distance between the top surface of the sample and the newly created focal point within the sample is called defocusing distance. Ultrasound is most strongly influenced by defects when the defect exists in the vicinity of the focal point. The ultrasound influenced by the defect propagates back to the transducer, and it is received by the same transducer. By using a pulse wave with a temporal resolution, the echo from the defect may be measured separately to the other echoes from the top and bottom of the sample, which are even stronger than the defect echo. As the focused transducer is mechanically scanned with a fine pitch in a plane parallel to the sample surface, the amplitude of the echo is recorded at each scanning position. An image is created by two-dimensionally mapping the amplitude of echo, showing the defect distribution in the vicinity of the focal depth. The image is called C-scan. By repeating the same procedure at different focal depths, the C-scans can be obtained for different focal depths.
Fig. 6 shows the experimental setup for obtaining C-scan image of the sample. With respect to the selection of focused transducer, as described above, a high frequency is capable of achieving both high sensitivity and high resolution, whereas it loses the penetration depth due to the high attenuation. Practically, the tradeoff between resolution and penetration depth needs to be discreetly considered. In this study, the focused transducer with a center frequency of 50 MHz was selected. The diameter is 6 mm and the focal length determined by the geometry of curved surface of the transducer is 20 mm. The sample was immersed in a water tank, and the focused ultrasonic transducer was partially immersed for normal incidence. The focused transducer was excited by a pulser (DPR500, JSR), which was controlled by a scanning and acquisition system (FlexScan, Insight, Japan). In this study, the cracks were indirectly visualized via the amplitude of bottom echo to achieve a high signal-to-noise ratio, since the direct scattering from the cracks was too small. In order to acquire C-scan images at various depths within the sample, the focal point was varied from the top surface of the sample to the bottom. For each defocusing distance, the mechanical scan was carried out over 20 x 20 mm² with a pitch of 0.1 mm. At each depth, the scan time for such a grid is on the order of minutes.

Fig. 7 shows the C-scan images obtained at different focal depths with the schematic illustrations. At the focal position on the top surface of the sample (Fig. 7a), multiple point-like responses were imaged in the area surrounding by the central hole (Fig. 7f). Most of them can be attributed to the small pits and rough surface due to local corrosion, since the positions of most responses were in good agreement with the positions of optically-observed ones. Although some of them may be attributed to small SCCs, it is not easy to identify them only in the C-scan image. As the focal position is moved toward the bottom surface of the sample (Figs. 7b-e), the multiple point-like responses became weak and ambiguous at the same positions in the C-scan images (Figs. 7g-j). For the deep focal points, some of them diminished. This is because the focal points were away from the top surface. This clearly shows that such scatterers existed only on the top surface of the sample. On the other hand, two SCCs extending from the central hole were clearly visualized as linear-shaped responses. In contrast to the aforementioned surface scatterers, the two SCCs were visualized consistently over all the focal depths within the specimen. This suggests that the SCCs penetrate through the thickness. Note that in Fig. 7i, the SCC2 was visualized as wider linear-shaped response. In Fig. 7j, SCC2 was observed as two linear responses. The results may suggest that SCC2 was slightly tilted or was branched around the surface A. Additionally, a third line is
observed on the edge of the hole. For this line, the contrast in the image does not appear to be as strong as the other two lines (SCC). Further inspection reveals that this third line is a scratch but without additional testing, this third line could have been a false positive for SCC.

Fig. 6. Experimental setup for ultrasonic C-scan images: (a) A tank with water where a focused transducer and the sample are immersed. (b) An enlarged photograph from the front that shows the appearance of ultrasonic focused transducer and the sample in a water tank.

Fig. 7. C-scan results obtained at various focal depths at 0.5-mm depth increments: (a)-(e) Schematic illustration showing the focal points on and within the sample. (f)-(j) Ultrasonic C-scan images obtained at the focal points shown in (a) to (e), respectively.
4. Detection Using Nonlinear Resonant Ultrasound Spectroscopy (NRUS)

Elastic waves are useful for nondestructive testing (NDT) applications because they are carried by the solid and interact with its constituents, including its defects. Imaging techniques based on linear ultrasonics (e.g., amplitude C-scan in Section 3) rely on the idea that ultrasonic waves are scattered by the defects, which alter the expected time of flight of the incident wave and/or its amplitude. These techniques typically require that the wavelength be smaller than the defect and that the defects create a large enough contrast of impedance within the solid. In this subsection, we focus on different effects, those stemming from nonlinear elasticity. Many material defects lead to nonlinear effects during the propagation of finite-amplitude ultrasonic waves, manifested as wave distortions in the time domain or generation of harmonics in the frequency domain [24-26]. Unlike techniques relying on linear scattering, these effects may be observed even when the wavelength is much larger (by orders of magnitude) than the defects. This fact is of practical importance for NDT applications since it may be and has been used for the early detection of defects in materials. In fact, it has been demonstrated that nonlinear signatures are far more sensitive to the presence of microscopic-sized defects, which are precursors to larger defects and eventually system failure, than linear signatures, including linear scattering, changes in the propagation speed of the ultrasonic waves, and linear attenuation [25,26].

NRUS is used in this study as a preliminary screening tool, to indicate whether or not a sample is damaged. Basically, NRUS consists of (i) vibrating a sample of finite size around one of its resonance frequencies at multiple amplitudes and (ii) tracking the dependence of the resonance frequency on the excitation amplitude. The resonance frequency of a pristine metallic sample should be independent of the excitation amplitude, as long as the maximum dynamic strain amplitude in the sample remains within the range of linear elasticity for the material studied. In the presence of cracks, dislocations, thermal damage, and possibly other defects, the resonance frequency starts decreasing as a function of strain, and very noticeably so when the strain goes above a certain level, typically near 10^{-6} at ambient conditions. Such a behavior has been observed in a variety of materials, including metals, rocks, and concrete. Broadly speaking, the drop in resonance frequency indicates material softening with increasing driving strain. However, the dependence of the resonance frequency on strain is not trivial [10,27] as it involves different
mechanisms of nonlinearity (i.e., classical and nonclassical) at various strain amplitudes. Of interest to this study is also the fact that the strength of the nonlinear response (e.g., dependence of the resonance frequency on vibration amplitude) is proportional to the crack density in the sample, as demonstrated by Van Den Abeele et al. [28] using thermally damaged composite samples. Hogg et al. [29] also recently found that $\alpha$ increases in welded steel rods with longer exposure to a hot, corrosive, aqueous MgCl$_2$ environment due to the suspected increase in SCC nucleation and growth with longer exposure.

In some previous studies conducted by some of the authors, the sample was a long thin bar with free boundary conditions and excited around the first mode of longitudinal vibration. The equation of motion and boundary conditions for the longitudinal modes of the bar of length $L$ ($-L/2 \leq x \leq L/2$) and mass density $\rho$ can be expressed as,

$$
\rho \frac{\partial^2 u(x,t)}{\partial t^2} = \frac{\partial}{\partial x} \left[ E(x) \frac{\partial u(x,t)}{\partial x} \right], \quad \varepsilon_{ss}(\pm L/2) = 0
$$

where $u(x,t)$ is the displacement of the bar in the longitudinal ($x$) direction and $E(x)$ is the Young’s modulus, which varies with position $x$ due to the presence of nonlinearity that depends on the strain $\varepsilon_{ss} = \frac{\partial u(x,t)}{\partial x}$.

In this paper, the sample has a complex geometry and set into complex motion by a contact transducer that is relatively large. The ideal conditions described by Eq. (1) are not met. However, damage detection is the priority in the study (rather than modeling the fine details of the physics leading to the nonlinear elastic behavior) and the key aspect of the experiment is to find a mode of vibration capable of exciting the damaged region. Such a mode of vibration can involve a longitudinal, torsional, and/or bending motion, as long that the cracks are set into motion to generate the sought nonlinearity.

NRUS experiments were conducted on two samples, the one shown in Fig. 1 with the two SCCs and another sample of identical shape in pristine conditions (without SCC) to be used as a
The experimental setup is shown in Fig. 8. A piezoelectric disc (PZT-5A ceramic with a diameter of 12.7 mm and a thickness of 2 mm) was epoxied near one corner of the sample and used as a source transducer to vibrate the sample. The transducer was driven with voltage signals generated by a function generator (National Instrument PXI-5406) and amplified 20 times by a voltage amplifier (TEGAM 2350). The vibrational response of the sample was measured with a laser Doppler vibrometer (laser head: Polytec PSV 400; vibrometer controller: OFV-5000; Decoder: VD-09 with max range of 200 mm/s/V and max frequency of 250 kHz) near another corner of the sample. The vibrational signals were digitized with a sampling rate of 10 MHz (National Instrument PXI-4122). The samples were vibrated with a sequence of harmonic voltage signals (i.e., sinusoidal bursts) around their fourth resonance mode with a frequency bandwidth of 100 Hz in steps of 2 Hz: from 7.48 to 7.58 kHz for the pristine sample and from 7.82 to 7.92 kHz for the sample with SCC. Each harmonic signal was played for 80 ms and the transient vibrational response was recorded during the last 40 ms of the source signal, to ensure that steady state conditions had been reached at each frequency step. Vibrational spectra were constructed from the harmonic responses, using heterodyne processing. The experiment was conducted for 24 excitation amplitudes ranging between 0.25 to 6 Vpp in steps of 0.25 Vpp, before amplification.

Fig. 8. Photograph of the experimental setup for NRUS measurements.
The resonance curves for the two samples are shown in Figs. 9a and b. Both samples exhibit a shift of their resonance frequency as a function of the source amplitude. It is also clear that the sample with SCC exhibits a more pronounced shift of its resonance frequency than the pristine sample. The first result is expected as all dynamic systems will eventually behave nonlinearly at sufficiently large dynamic amplitudes. In this case, the piezoelectric transducer and epoxy bonding between the transducer and the sample are most likely the cause of the nonlinearity (shift of resonance frequency) observed in the pristine sample. The second result is caused by the presence of SCC.

Fig. 9. Magnitude of the spectra of the particle velocity measured for 24 source amplitudes around the fourth resonance mode of vibration of the sample: (a) pristine sample; (b) sample with SCC.
Quantification of the nonlinearity is done by analyzing the relative shift of the resonance frequency as a function of the maximum amplitude of the volumetric strain in the region of interest (the boundary of the hole at the center of the sample). In the experiments, the vibration is measured at one point only. The relationship between the particle velocity at that point and the maximum strain amplitude is established with numerical modeling, based on the finite-element (FE) method implemented in the commercial software package COMSOL Multiphysics. The FE model consists of the sample instrumented with the source transducer, with geometry and material properties shown in Fig. 10. The computational domain is discretized into 34770 quadratic tetrahedral elements with a maximum element size of 0.9 mm, resulting in a model with 171996 degrees of freedom. The first 5 resonance frequencies and corresponding mode shapes of the sample were computed. Fig. 11 shows the magnitude of the displacement and volumetric strain for these modes. A frequency sweep was also conducted experimentally between 1 and 11 kHz to identify the resonance frequencies and check the validity of the model. The spectrum measured in this experiment is shown in Fig. 12. The agreement between measured and predicted resonance frequencies is excellent considering that the epoxy (bonding between transducer and sample) was not modeled and nominal (as opposed to measured) material properties were used in the simulations. The numerical model indicates that the ratio of the particle velocity at the measurement point (where the laser beam is pointing) and the volumetric strain at the boundary of the center hole (where the cracks are located) is approximately equal to 18000 m/s.

<table>
<thead>
<tr>
<th>304 Steel</th>
<th>Mass density, ( \rho = 8000 \text{ kg/m}^3 )</th>
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<tr>
<td></td>
<td>Young’s modulus, ( E = 193 \text{ Gpa} )</td>
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<td></td>
<td>Poisson’s ratio, ( \nu = 0.3 )</td>
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<tr>
<th>PZT-5A</th>
<th>Mass density, ( \rho = 7750 \text{ kg/m}^3 )</th>
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<td>Elastic Tensor: ( c^t = 10^3 )</td>
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<td>( \begin{bmatrix} 120.3 &amp; 75.2 &amp; 75.1 &amp; 0 &amp; 0 &amp; 0 \ 75.2 &amp; 120.3 &amp; 75.1 &amp; 0 &amp; 0 &amp; 0 \ 75.1 &amp; 75.1 &amp; 110.9 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 21.1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 &amp; 21.1 &amp; 0 \ 0 &amp; 0 &amp; 0 &amp; 0 &amp; 0 &amp; 22.6 \end{bmatrix} \text{ Pa} )</td>
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Fig. 10. Geometry of the model and material properties used to compute the resonance frequencies and corresponding mode shapes of the sample instrumented with the source transducer.

Fig. 11. First five resonance frequencies and corresponding mode shapes of the sample instrumented with a source transducer.

Fig. 12. Magnitude of the spectrum of the particle velocity measured near a corner of the sample for low-amplitude source signals. A low-amplitude source signal ensures that the vibrational response is linear.
Using the results from the numerical analysis, it is now possible to reduce the data plotted in Fig. 9. The relative shift of the resonance frequency as a function of the volumetric strain (estimated at the boundary of the center hole) is shown in Fig. 13 for the two samples. The slope of the linear portion of the data is the parameter of nonclassical nonlinearity $\alpha$. For the pristine sample, $\alpha = -45$. For the sample with SCC, $\alpha = -185$, which represents an increase by a factor of 4 compared to the pristine sample. Given that the samples had the same geometry, were instrumented with the same transducers, and were driven with the same signals, this large increase can only be attributed to the presence of cracks.

![Graph showing relative shift of resonance frequency as a function of volumetric strain for pristine and sample with SCC](image)

Fig. 13. Magnitude of the spectrum of the particle velocity measured near a corner of the sample for low-amplitude source signals. A low-amplitude source signal ensures that the vibrational response is linear.

In the intended application of using NRUS to detect the presence of SCC on a storage cask, NRUS measurements can be made with the same equipment, over regular time intervals, to determine whether $\alpha$ is increasing with time or not. It is likely that experiments conducted on pristine casks and then on damaged casks may be needed to help quantify the $\alpha$ value, which, if exceeded, will suggest the presence of SCC, though perhaps numerical models can provide this information as well. Since NRUS requires the measurement of resonance curves at several amplitudes, including low enough amplitudes to assume linear elasticity, changes in the overall wave speed in the sample
are taken into account. Thus the NRUS technique does not rely as heavily on the direct comparison to a pristine sample nor does it depend on the sample’s wave speed remaining constant, but rather \( \alpha \) depends on the quantity of cracking present, as previously discussed [28,29]. Note that in principle, NRUS may be used for crack localization, as suggested by Abeele [30] and demonstrated by Ohara et al. [31]. In brief, the localization of nonlinear scatterers can be achieved by changing the mode order, thus changing the location of the nodes and anti-nodes of vibration. While this is a relatively simple process for small samples with simple geometries, it could become a daunting task if the crack size is orders of magnitude smaller than the host structure and the geometry of the structure is complex.

5. **Linear Elastodynamics Gradient Imaging Technique (LEGIT)**

As part of this study, a new technique was developed, namely, Linear Elastodynamics Gradient Imaging Technique (LEGIT). For LEGIT, a transducer inputs acoustic energy into the sample in the form of a pulse. The interaction of the cracks in the sample with the acoustic waves results in discontinuities at the crack locations, which can be imaged by measuring the response of the sample using a laser vibrometer.

The experimental set-up is shown in Fig. 14. A piezoelectric transducer (PZT-5A ceramic with a diameter of 12.7 mm and a thickness of 2 mm) was epoxied near a corner of the sample. Reflective tape was applied to the sample over the region where the two SCCs were known to be located to increase the Signal to Noise Ratio (SNR). The input signal was generated from an internal arbitrary waveform generation card in the scanning laser vibrometer (Polytec PSV-3D-500 in 1D mode). The signal was then amplified 100 times by a voltage amplifier (TEGAM 2350) before being input to the piezoelectric transducer.
Fig. 14. (Left) Entire experimental set-up for LEGIT with data acquisition system shown. Only the top laser head was used to measure the out-of-plane velocity component. (Right) Side view of experimental setup showing the sample, inset is a close up view of the sample. The piezoelectric transducer is not visible because it is on the backside of the sample.

To maximize the response of the sample, the input signal was centered around one of the resonance frequencies of the sample. The resonance peaks of the sample were found by inputting a burst chirp with frequencies from 20 kHz to 300 kHz into the sample and observing the response at various locations on the sample. An example of a frequency spectrum from a point on the sample is shown in Fig. 15. Based on the measured spectrum, a pulse at 175 kHz with 157 cycles was chosen as the input signal.
Fig. 15. Frequency spectrum for input pulse with frequencies from 20 kHz to 300 kHz. The resonance frequency of 175 kHz was chosen as the frequency for the input signal.

Using the Polytec acquisition software, a scan grid was defined around the region with the two SCCs. Fig. 16 shows the defined scan grid. The grid contained 6516 points and was 15.5 mm in length by 7.2 mm in height, resulting in a resolution of approximately 0.12 mm. At each point on the scan grid, the pulse was input into the sample and the out of plane velocity response was measured using the scanning laser vibrometer (Polytec PSV-3D-500 in 1D mode). Only the top laser head was used to measure the out of plane velocity component. Data was collected at 3.25 MHz for 10 ms. Each pulse was allowed to dissipate before moving to the scan point.
Fig. 16. Scan grid with 6516 points, with a resolution of approximately 0.12 mm.

To process the data, the time domain data was taken to the frequency domain. Fig. 17 shows a frequency spectrum from one point on the scan grid. The spectrum was integrated around the fundamental mode at each point on the scan grid to build an image of the defect locations. Next, the gradient was taken in the $y$-direction to identify the discontinuities caused by the interaction of the SCCs with the acoustic waves (Fig. 18a). As can be seen in Fig. 18c, comparing LEGIT results to that obtained with vibrothermography (Fig. 18b) (see Section 5), shows the identified crack locations are in agreement.

Fig. 17. Frequency spectrum for one point on the scan grid, harmonic generation from the SCCs is evident in the spectrum.
Fig. 18. Results from LEGIT (a) image from taking the gradient in the $y$-direction of the integrated fundamental frequency. The large red area and the discontinuity on the left side of the hole correspond with the crack locations from vibrothermography (Section 5) (b). Overlaying the image from LEGIT and the vibrothermography (c) shows that the identified SCC locations agree well.

6. Vibrothermography

Vibrothermography is a NDE method used to detect surface and near surface defects in materials. While this method was first used to find cracks and delaminations in composite materials [11], its applications have since been expanded to detect cracks in metals [32]. Vibrothermography offers advantages in that it is able image large areas for cracks efficiently. In order to standardize vibrothermography, work is being done to understand the effects experimental variables have on the probably of detecting a defect [33].

Vibrothermography utilizes the conversion of mechanical energy to heat to image damage. At defect locations, heat is converted to mechanical energy. The physical heat-generating mechanisms of cracks are frictional heating from crack faces rubbing and/or clapping, plastic deformations from crack growth, and viscoelastic heating due to stress concentrations in a material. Friction as a heat-generating mechanism has been supported by numerical models that couple thermo-
mechanical analysis to predict the temperature distribution on fatigue cracked steel samples [34]. Renshaw et al. have confirmed all three of these heating mechanisms through experiments that isolated each mechanism for careful individual study [12]. Viscoelastic heating, however, has been found to be a dominant mechanism in polymer based composite materials [11], and therefore is not considered a dominant heat generation mechanism in the current study. It is also important to note that friction can induce plastic deformation along a crack as the faces are being clapped together. The amount of heat generated is influenced by the external stress state and whether the crack is open or closed. As the external stress is increased, experiments have shown that heat generation moves to the edges of a crack [35]. If a crack is fully open or fully locked by external stress, vibrothermography will likely not detect the crack due to lack of heat generation.

To image defects with vibrothermography, samples are resonated using a mechanical excitation device, e.g. piezoelectric transducers, electromagnetic shakers, or ultrasonic transducers, and imaged with an infrared (IR) camera. In the current study, a piezoelectric transducer was epoxied to a corner of the sample following the setup used for the NRUS testing (see Fig. 8). A frequency sweep over a wide frequency band indicated that the maximum vibration amplitude was reached near 175 kHz. This frequency was selected for the test to create the maximum thermoelastic effect while ensuring that the sample would remain in the elastic regime and the crack would not grow further. The infrared emission in the region of interest was recorded for 10s at 120 frames per second using a FLIR SC8200 IR. The source transducer was driven at 200Vpp for 7.5s, 0.5s after the acquisition had started (for the last 2s of the acquisition, the source was off). The data acquisition and processing were controlled by a system (hardware + software) developed by Thermal Wave Imaging. It takes less than 30s between the start of the experiment and the completion of the data post-processing displayed below.

Fig. 19 shows 3 snapshots of the thermal field in the region of interest. Some data processing is required to obtain these images. The camera originally provides a map of the temperature distribution for each frame of the video acquisition. The evolution of temperature with time, \( T(t) \), is noisy. Noise is removed by fitting \( T(t) \) with a 10th-order polynomial at each data point of the map. The contrast is then enhanced by taking the first derivative with respect to time of the fitted \( T(t) \). Any abrupt change in temperature will be enhanced by taking the derivative. The evolution of temperature as a function of time at three points on the sample is shown in Fig. 20.
Fig. 19. Snapshots of the first derivative with respect to time of the temperature at each point of the scan region due to a continuous sine wave at 175 kHz. Snapshots taken at (a) 0.5s, (b) 4.5s, and (c) 9.5s into the 10s acquisition.

Fig. 20. Evolution of temperature as a function time at three points in the scan region. The location of the points (1,2,3) is indicated in Fig. 10(a).

7. Synchrotron X-ray tomography

X-ray tomography is used in this study to provide “ground-truth” measurements. The technique of X-ray tomography is similar to Computerized Tomography (CT) scans used in the medical
industry to produce 3-D representations of the body [36]. A sample is rotated around an axis perpendicular to the high energy beam of X-rays and a series of 2-D projections are collected at the different angles of rotation [36]. The detectors are usually composed of a scintillator material along with a CCD camera [36]. The high brilliance of high energy X-rays allows for quicker scans compared to other X-ray tomography sources such as tungsten filament [37]. A filtered back-projection algorithm is then used to create 2-D images from the projections based on differences in phase contrast [36]. Phase contrast can arise from differences in X-ray absorption which can be altered by differences in materials, holes, cracks, and pores [37]. Further filtering using Fast Fourier transforms can be used to remove artefacts [38]. The 2-D images are then stacked and 3-D representation of the crack can be produced using a reconstruction software like Avizo ®. Various researchers have shown how X-ray micro tomography can be used to create 3-D representations of cracks with resolutions on the order of microns [13, 37, 39].

Although X-ray micro tomography allows for the 3-D reconstruction of cracks in materials with micron level resolution, this technique still has its limitations. Some of the limitations arise from the technique of phase contrast while others arise from the limited resolution. Features of the crack, which can include small secondary cracks and sharp crack tip, can be missed in the tomography scan due to their small size relative to the resolution of the scan [40]. Crack tip geometry is an important parameter for understanding crack propagation so lacking the insight into the crack tip radius can hinder a better understanding [40]. Additionally, cracks with large differences in aspect ratio can lead to unequal contrast at different projection angles which reduces resolution of the crack [40]. With regards to the technique of using synchrotron X-rays and using phase contrast, small samples (<10 mm) must be used to allow enough X-rays to pass through the sample [40]. Generally, samples must contain a square or circle cross section to avoid drastic changes in contrast with rotation [40]. From the parallel beam of X-rays, crack edges can cause fringes in the image to appear, resulting in a reduction of resolution in the area [41]. The formation of artifacts in the tomography scans adds additionally limitations to the technique [38]. Artifacts arise due to the non-linear response of the detectors as well as dust that can accumulate on the optics or scintillator due to the constant bombardment of high energy photons on materials [38]. Careful analysis of the scans is needed to identify artifacts that usually appear as rings in the 3-D model [38]. For in-situ
scans involving various equipment, wobbling of the sample can become more common during the rotation of the sample which can lead to blurry areas in the sample if not corrected [42].

7.1 Microstructural Characterization
The morphology of cracks and pitting sites were inspected by optical microscopy and SEM (FEI Quanta 3D FEG). Elemental composition around surface crack and pitting sites were also determined by Energy-dispersive X-ray Spectroscopy (EDS), using an X-ray detector (Oxford Instruments) coupled with SEM. EDS, when combined with these imaging tools (SEM), can provide spatially resolved elemental analysis from areas as small as 0.1 ~ 3 microns. The impact of the electron beam on the sample produces X-rays that are characteristic of the elements present on the sample. EDS analysis was used to map out the lateral distribution of elements from the imaged area on the sample surfaces. In an EDS map, bright zones indicate enrichment of an element, whereas dark zones shows depletion of that element.

7.2 X-ray Microtomography
The microtomography experiment was conducted at the high-energy synchrotron beamline 1-ID-E at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), with a beam size of 2.1×1.3 mm. Measurements were collected with a monochromatic synchrotron X-ray beam at an energy of 90.55 keV. The specimen was mounted on a rotational stage that enabled the specimen to be rotated through a continuous 360° range with radiography collections 0.2° intervals along the rotation axis. The sample stage and detector were carefully calibrated to yield pixels rows perpendicular to the rotation axis of the sample, which facilitates reconstruction. This series of projections was reconstructed with a filtered back projection algorithm to obtain a dataset of a 3D isotropic voxels (size 1×1×1µm) representing voxel-average X-ray linear absorption coefficient. For the full crack, two vertical sample volumes were stacked.

Indeed, since the sample volume containing the full size of the crack cannot be included in one tomographic scan, two groups of tomography datasets (with partial overlapping) containing partial of the same crack were measured.
Fig. 21a is a schematic drawing of the SS304-09A compression washer with a through-hole geometry which shows two cracks. Fig. 21b shows the 3D iso-surface rendering of two layers (layer-1 and layer-2) of the crack on the top of the hole. These 3D image datasets with partial overlapping are then matched based on image registration to form a larger sample volume containing the full crack.

Fig. 21. Tomographic scan of crack in SS304-09A compression washer. (a) Schematic drawing of a SS304-09A compression washer with a through-hole geometry (6.8mm diameter) and two cracks. (b) 3D isosurface rendering of two tomographic datasets (with partial overlapping) of the same crack. (c) Projection of layer-1 onto the YZ-plane. The unit in all axes is μm.

7.3 Image filtering, registration and volume rendering
Prior to the image registration, a pre-treatment of the 3D tomography data to remove the artefacts was required. As shown on the 2D slice (XY-plane) in Fig. 3b, there are many bright horizontal lines, which cross the crack region. Those bright horizontal lines on the 2D slices are actually horizontal planes on XY-planes when observed on 3D volume rendering, as shown in Fig. 3a. Due
to the large width (25mm) of the specimen, X-rays are fully absorbed for a range of angles as the thick direction aligns with the beam direction. Consequently, reconstruction of the tomographic data results in artefacts that appear as bright horizontal lines (cross-hatched shading in Fig. 3b).

A filter module based on fast Fourier transform algorithm is used to remove these artefacts on the 2D slices. Fig. 22c shows the slice after performing filtering to the slice shown in Fig. 22b. After removing artefacts on the reconstructed 3D tomography datasets, overlapping sample volumes (layer-1 and layer-2) are matched based on image registration. Image registration procedure is based on feature detection, feature matching, mapping function design, and image transformation and resampling [43]. Crack features are used to align the two volume elements to reconstruct the entire crack geometry.

Fig. 22. 3D image filtering. (a) 3D volume rendering of the crack (layer-1) before image filtering. The red dash rectangle indicates the region with artefacts. (b) Ortho slice (slice 1020 in XY-plane) before filtering, and (c) the same slice obtained by Fourier transform filtering to remove stripes (artefacts) in the horizontal direction in B.

Visualizing the crack is achieved by thresholding the linear absorption coefficient (LAC) for each voxel [44]. Accurately extracting the whole crack volume however depends on the choice of
threshold in the 16-bit grayscale image; the threshold value selected will determine the interface position between the crack and the matrix [45]. For this investigation, an intermediate value was taken corresponding to the valley between the air and steel absorption peaks in the 16-bit LAC distribution. Finally, a ‘seed’ growth technique for voxel continuity was applied to eliminate noise, to create a fully connected 3D voxel set representing the crack and interface. Those voxels that belong to the crack are set at fully opaque, whereas the voxels belonging to the matrix are set at fully transparent.

### 7.4 3D Visualization and Analysis of the Crack

The full 3D crack reconstruction yields a 3D volume (Fig. 23) rendering of the crack with multiple crack branches. The volume rendering of the crack was aligned to be parallel to the YZ-plane. The main crack volume is labelled with blue colour. Crack branches are labelled with different colours in order to differentiate them from the main crack. The extracted crack volume is projected onto YZ-plane for both positive X (Fig. 23b) and negative X (Fig. 23d) direction, which is perpendicular to the loading direction. Optical image (Fig. 23c) is used to compare the surface crack with the 3D crack morphology. The corrosion pits (1-2) and crack jumps (3-4) are matched between optical surface observation (Fig. 23c) and 3D tomography results (Fig. 23B-D). (1) and (5) indicates the edge of the crack appears on the sample surface.
Fig. 23. (a) 3D volume rendering of the crack with multiple crack branches. A projection of the crack volume onto YZ-plane on (b) positive X direction and (d) negative X direction. a - e indicate five different crack branches labelled with different colours. The unit in each axis is µm. (c) Microscope image showing the morphology of the crack on the sample surface. (1) and (2) show pits on the sample surface, (3) and (4) show crack jumps, (5) indicates the edge of the surface crack.

To observe the crack branches in more details, 2D ortho-slices with progressively increasing depth for crack branch-a and -c were carefully selected and extracted from the 3D volume. Fig. 24A shows a selected crack volume from 1100 to 2000 in Z-axis to show the branch-a (red). Figs. 24(a)-(e) show 2D slices from slice 320 to slice 560 on XZ-plane (see Fig. 23), with interval of 60 slices (60µm). The data volume from 1100 to 2000 is cropped to show the crack branch-a. The white solid arrow and black arrow indicate the upper and lower parts of the crack branch-a in Fig. 23, and the white dash arrow is a part of the main crack.

Crack branch-a is also observed on XY-plane. Fig. 25(a)-(e) are 2D slices from slice 1480 to slice 1800 (XY-plane), with interval of 80 slices (80µm). The white solid arrow indicates the crack branch-a in Fig. 23.
Fig. 24. Projection of the crack onto (A) YZ-plane and (B) XZ-plane to show the branch-A (red), with a range of 1100-2000 in Z-axis. (a)-(e) are 2D slices from slice 320 to slice 560 on XZ-plane, with interval of 60 slices (60µm). The white solid arrow and black arrow indicate the upper and lower parts of the crack branch-a, and the white dash arrow is a part of the main crack. The unit in each axis is µm.
Fig. 25. Projection of the crack onto (A) YZ-plane and (B) XY-plane to show the branch-a (red), with a range of 1100-2000 in Z-axis. (a)-(e) are 2D slices from slice 1480 to slice 1800 on XY-plane, with interval of 80 slices (80µm). The white solid arrow indicates the crack branch-a. The unit in each axis is µm.

2D ortho-slices of crack branches-b and -c with progressively increasing depth are also carefully selected and extracted from the 3D volume. Fig. 26A shows a selected crack volume from 800 to 1400 in Z-axis to show the branch-c (green) and branch-c (blue). Fig. 26(a)-(e) show 2D slices from slice 520 to slice 760 on XZ-plane, with interval of 60 slices (60µm). Fig. 27(a)-(e) are 2D slices from slice 960 to slice 1280 on XY-plane, with interval of 80 slices (80µm). The dash arrow and solid arrow indicate the crack branch-b and -c, respectively. Fig. 26(a) is a slice (Y=520, XZ-plane) near the edge of crack branch-b and -c, where two small branches are formed near the main crack. As the slice depth increase from 520 (a) to 640 (c), the length of crack branches increase and the branches reach deep into the matrix. The section of the main crack between branch-b and
c start to diminish after slice depth 640 (c) and disappear in (d), where the branch-b become a part of the main branch.

From 2D ortho-slices on XY-plane as shown in Fig. 26(a)-(e), the branch-c (white solid arrow) formed a new sub-branch in (b) and start to diminish in (e). The edge of branch-b (white dash arrow) is shown in (a) as a single branch, but three sub-branches are formed in (c). Those three sub-branches converged into a main crack with small branches reach into the matrix, as shown in Fig. 26(d) and (e).

Fig. 26. Projection of the crack onto (A) YZ-plane and (B) XZ-plane to show the branch-b (green) and branch-c (blue), with a range of 800 - 1400 in Z-axis. (a)-(e) are 2D slices from slice 520 to slice 760 on XZ-plane, with interval of 60 slices (60µm). The dash arrow and solid arrow indicate the crack branch-b and -c, respectively. The unit in each axis is µm.
Fig. 27. Projection of the crack onto (A) YZ-plane and (B) XY-plane to show the branch-b (green) and branch-c (blue), with a range of 960 - 1280 in Z-axis. (a)-(e) are 2D slices from slice 960 to slice 1280 on XY-plane, with interval of 80 slices (80µm). The dash arrow and solid arrow indicate the crack branch-b and -c, respectively. The unit in each axis is µm.

8. Conclusion

In this paper, we reported the finding of an extensive NDT program conducted on a small sample of stainless steel with two cracks of mm-scale sizes. This is a preliminary study aimed at evaluating the capabilities of several NDT tools that could eventually be deployed in the field to image SCC in stainless steel canisters. There is a tradeoff between the ease of implementation (and applicability in the field) and level of detail that can be obtained from the technique. For instance, a detailed 3D image of the crack could be obtained with X-ray tomography, but this technique cannot be deployed in the field. On the other hand, NRUS was shown to be a powerful and easy to implement tool for detecting the presence of one or multiple cracks but cannot be used to locate or image the cracks. Ultrasonic C-scans could image the cracks and their penetration depth. However, the probe needs to be coupled to the structure with a fluid, which would require some
engineering design if this technique were to be deployed inside the concrete overpack. More importantly, C-scans cannot differentiate a cracks from a notch or surface scratch because of the physics involved in the imaging processing (echoing of the incident ultrasonic waves). Vibrothermography and LEGIT provide very similar images of the cracks and are transparent to the presence of surface scratches. These two techniques are based on the same physical mechanism, namely, the clapping (opening and closing) of the cracks interacting with the incident ultrasonic waves. Vibrothermography exploits temperature changes whereas LEGIT exploits the generation of harmonics by the cracks for detection and wave-field discontinuities at the crack for imaging. Vibrothermography cannot be currently deployed in the field because of the geometrical constraints in the concrete overpack. The infrared camera would have to be miniaturized and shielded from the radiations for the technology to be deployable. However, LEGIT could be deployed with some changes to the setup and equipment. The large scanning laser head used in our experiments could be replaced by a fiber-optic sensor head (e.g., the OFV-55x device from Polytec). Such a device does not have built-in scanning capabilities but could be moved and operated by a dedicated robot to scan the surface. The transducer glued to the surface in our experiment could be replaced by a non-contact EMAT transducer, which was already accomplished elsewhere [5,6]. The engineering of such technologies is beyond the scope of this study. Future work could include a similar study on much larger samples, as an intermediate step between the current study and the field application.

Acknowledgements
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Chapter 8
An application of stochastic modeling to pitting of Spent Nuclear Fuel canisters

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**ABSTRACT**

Chloride induced stress corrosion cracking (CISCC) is one of the main factors affecting the integrity of used nuclear fuel in dry storage canisters, especially at coastal sites. CISCC has complex interactions associated with environment, stress and materials properties. This paper is focused on the development of probability distribution functions for maximum pit depth based on experimental data created at Lawrence Livermore National Laboratory (LLNL) that have not been fully analyzed before. The LLNL report outlined the key variables of pit initiation, termination and growth rate that may lead to CISCC, with the final aim of prediction of canister life and optimization of the time interval inspection of the canisters. The key parameters characterizing the probability distributions of pits at each stage depend on environment, material susceptibility conditions, and residual stress intensity. A basic stochastic approach to estimate probability distributions based on the median and maximum pit depths observed in experimental data succeeds in reproducing the experimental results, and can be used to estimate the distribution of maximum depth at future times.

1. Introduction and motivation

Currently, Spent Nuclear Fuel (SNF) is stored in two types of environmental storage conditions: 1) submerged in water in pools at reactor facilities, and 2) in dry storage at Independent Spent Fuel Storage Installations (ISFSIs), adjacent to reactor facilities. Generally after a few years of cooling time, SNF is removed from the water pool and transferred to helium-filled stainless steel canisters in passively ventilated dry storage systems.

Decisions have been made not to pursue Yucca Mountain as a long-term geologic repository storage facility for SNF and to cancel the construction of a reprocessing facility in the 1980s due to proliferation risks. As a result, interim dry storage facilities for long-term storage have been vital for the immediate future of nuclear energy technology. The Nuclear Regulatory Commission (NRC) and DOE have identified potential deterioration mechanisms for steel canisters containing the SNF in dry storage that require detailed research and investigation. This will have an impact on the performance of long-term interim storage under the normal and extreme environmental conditions experienced during the duration of this storage. The prediction and monitoring of canister corrosion processes while in storage can provide important information for the assessment of interim storage performance and the safety to the public.

One of the primary concerns with respect to the long-term performance of storage casks is the potential for corrosion initiation due to deliquescence of salts deposited on the canister surface as aerosols; in regions of high residual weld stresses this may lead to localized stress corrosion cracking (SCC). Dust and aerosols in the air that are drawn through ventilation openings in the overpacks of passively-ventilated dry canister storage systems may be deposited on the stainless steel canister outer surfaces. Under these conditions, localized corrosion attack can occur. Chloride-induced stress corrosion cracking (CISCC) of welded zones is of special concern, as it is a well-documented mode of attack for austenitic stainless steels (including 304SS and 316SS) in marine environments (Kain, 1990), and many independent spent fuel storage installations (ISFSIs) are located in coastal areas. Recent canister inspections (EPRI, 2014; Bryan and Enos, 2014) have shown that chloride salts are present on the surface of in-service canisters in near-marine settings. However, canister surface inspections of sufficient resolution to detect SCC have never been carried out, because access to the canister surfaces through vents in the overpacks is extremely limited, and high radiation fields make removal of the canisters from the overpacks undesirable.

2. CISCC in dry storage canisters

SCC has been a research topic for many years. However, only a fraction of the large body of available research is relevant to the unique
conditions of dry storage canisters. The time scale from pit initiation and growth, transition to crack, and crack growth rate is still the subject of much research. The current knowledge related to dry storage canisters is summarized based on the three necessary conditions for CISCC (Environment, Susceptible Material, and Residual Stress).

2.1. Environmental conditions

In order for an environment to be aggressive, two conditions must be met: a corrosive chemical species must be present and aqueous conditions must exist. Other aggressive species may be present as well (e.g., high atmospheric concentrations of SO₃). This paper focuses on chloride species; that is, only CISCC is being considered in this study. An aqueous condition can occur as the canister cools, as salts deposited as aerosols on the canister surface deliquesce (absorb water) to form brines. The quantity of deposited chloride on canister surface is an important factor of CISCC. Estimates of the minimum amount of chloride to support SCC include 0.3 g/m² (Shirai et al., 2011); 0.1 g/m² (Albores-Silva et al. 2011); and 0.056 g/m² (NRC 2014). Other authors have reported CISCC at even lower salt loads, from 0.02 to 0.005 g/m² (Tokiwai et al., 1985; Taylor, 1994; Fairweather et al., 2008). Some studies have indicated that the salt surface load also has an impact on crack growth rate, as it affects the current-carrying capacity of the brine layer and the ability of the cathode, outside of the pit, to support corrosion at the anode, within the pit. This approach has been proposed for estimating maximum pitting penetration depths in several recent papers (for example, Chen and Kelly, 2010; Woldemedin and Kelly, 2014; Krouse et al., 2014). To assess whether chloride is present on the canister surface requires knowledge of: (1) the composition of deposited salts and amount of chloride being de-posited; and (2) the relative rates of chloride deposition versus chloride loss (e.g., via acid degassing) through time.

2.2. Susceptible material

Austenitic stainless steel is the regular material used in canister of dry storage casks, including Types 304, 304L, 316, and 316L, with the predominant material being Type 304 stainless steel. These materials are susceptible to SCC in aggressive environments. It occurs readily in experimental tests with deliquesced sea-salts (e.g., Nakayama, 2006; Tani et al., 2009; Mintz et al., 2012; Prosek et al., 2009, 2014), so experimentally determined material property factors such as the stress intensity factor (K), degree of sensitization (Rₛᵣ), oxygen concentration (O), the mass of chloride per unit surface area (m₉Cl), and the solution pH. Most of these variables fluctuate randomly. Therefore pit initiation and growth rate are subjected to random mechanisms. The authors are not aware of any theoretical physical models that can provide adequate prediction for various conditions or pit initiation and growth rates as stated above.

3. Pit initiation and growth

In most of the models, pitting initiation is based on nucleation-type theory in conjunction with the statistical methods used to describe rare-event processes when conditions for SCC are met (Turnbull et al., 2006). Two sources of information are available with respect to pit occurrence:

- Accelerated laboratory experiments: a high temperature and aggressive environment are used leading to fast (within days) occurrence of pits, although fast pitting, especially for heavily sensitized materials, is reported in the open literature (The data analyzed in this paper is of this type).

- Observation at ambient temperatures: these observations generally lead to slower occurrence of pits.

However, very few studies have been reported in the literature regarding the environment of interest for storage canister surfaces, and what is usually reported is the maximum pit depth observed rather than the evolution of pit depth as a function of time, rendering the model by Turnbull and Zhou (2004, 2006) difficult to parameterize for the present study. Rather, a statistical approach for the formation of stable pits is used in most models and in also this paper. One of the challenging tasks from a statistical point of view is to perform experimental work to parameterize a pitting initiation and growth model, to better estimate incubation times prior to the transition of pits to stress corrosion cracks. The CISCC incubation times are a major uncertainty in predictive models for SCC.

3.1. Pit growth model

A typical pitting growth model is described by Turnbull et al. (2006). It has the form:

$$\frac{dx_{\text{pit}}}{dt} = \alpha_{\text{pit}} f_{\text{pit}}$$

where $x_{\text{pit}}$ is pit depth, $t$ is time after initiation, $\alpha_{\text{pit}}$ is a scaling factor, and the exponent $f_{\text{pit}}$ is, in part, a function of the pit geometry and determines the shape of the growth curve with time for various environmental and materials conditions. Parameters $\alpha_{\text{pit}}$ and $f_{\text{pit}}$ are generally determined experimentally for a given system and environmental conditions. Pitting corrosion rates are strongly affected by temperature, pH, (Relative Humidity) RH, and chloride concentration of the bulk solution (Shoji and Ohnaka, 1989; Ernst and Newman, 2002; Lu et al., 2008; Chen and Kelly, 2010; Asaduzzaman et al., 2011; Saadawy, 2012; Cook et al., 2011; Davenport et al., 2014; Krouse et al., 2014; Vagbhathari and Gopalakrishnan, 2014), so experimentally determined rates would only be relevant for specific system. In reality the deliquesced sea-salts, undergo randomly variable periodic evaporation and dry out at canister surface. Pits growth rates are a function of many different parameters and can be expressed in the following general form:

$$dx_{\text{pit}} = \alpha_{\text{pit}}(T)(K)(R_{\text{s}})(f(\overline{C}))(f(\overline{O}))(f(\overline{m}_9\overline{Cl})) \ldots dt$$

where $\alpha_{\text{pit}}$ is the pit growth amplitude factor (at a fixed reference set of conditions), which can be modified by many other factors, including (1) material property factors such as the stress intensity factor (K), degree of sensitization (Rₛ), and yield stress (σₚ); (2) chemical factors such as temperature (T), chloride concentration ([Cl⁻]), oxygen concentration (O), the mass of chloride per unit surface area (m₉Cl), and the solution pH. Most of these variables fluctuate randomly. Therefore pit initiation and growth rate are subjected to random mechanisms.
3.2. Causes of pit death

Pits can become unstable when local conditions change, and repassivation, or “death” of the pit occurs. Three causes of pit death are now described.

- Death by old age – the pit demands more and more resources from that external surface in terms of oxygen reduction, which the external surfaces cannot deliver and, eventually, the pit dies (starves to death).
- Death by conflict – neighboring pits compete for the same resources, which are insufficient to keep both pits alive. The fittest survives, the weakest dies.
- Death by misadventure – some change on the external surface prevents continued oxygen reduction (e.g., drying of the surface) and the pit dies. All these activities are subjected to random processes.

The rest of this paper is organized as follows. The experimental data is presented, with the intention to explore the relationships between the measured physical parameters applied potential, pH and exposure time, and the rates of pit initiation and growth. Then the time-dependent growth rate and distribution of the maximum pit depth are estimated, using both the bootstrap and generalized extreme value distributions. Finally, an extrapolation is performed for the experimental data beyond the experimental time frame, with an estimation of upper and lower confidence bounds. Conclusions drawn from the stochastic data analysis are presented at the end of the paper.

4. Description of experimental data

Henshall (1996) reported the results of an experiment in which 1 cm² samples of Incoloy 825 were immersed in acidified brine (5% NaCl) at 90 °C for varying exposure times and amounts of applied electrochemical potential Eapp. The values of Eapp, exposure time, and pH are given in Table 1. The resulting numbers of pits, along with median and maximum depths, are presented in Table 2.

The time to pit initiation, and once initiated, the growth rate are modeled. It should be noted that not all pits are stable. However, since there are only a limited number of counted pits, it is reasonable to assume that all the counted pits are stable. Ideally, the initiation and growth rates would be modeled as functions of Eapp, pH, and exposure time. However, because there are only five samples, the effect of Eapp, pH, and exposure time would have to be fairly strong to specify a precise mathematical model. Plots shown below suggest that this is not the case.

Let T represent the exposure time and n the number of pits. Figs. 1–3 are plots of the observed initiation rate n/T versus, Eapp, pH, and T, respectively.

Roughly speaking, as suggested by Henshall (1996), the initiation rate increases with Eapp. However, Fig. 1 shows that the two samples with identical values of Eapp (382) have quite different initiation rates. These two samples have nearly the same pH as well (2.66 and 2.64). These results suggest that either there is a large random variation in initiation rate, growth rate is affected by factors not measured, or that initiation rate increases with exposure time. This last possibility will be addressed in our discussion of Fig. 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eapp (mV SHE)</th>
<th>Exposure Time (min.)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>372</td>
<td>480</td>
<td>2.67</td>
</tr>
<tr>
<td>2</td>
<td>382</td>
<td>120</td>
<td>2.66</td>
</tr>
<tr>
<td>3</td>
<td>382</td>
<td>218</td>
<td>2.64</td>
</tr>
<tr>
<td>4</td>
<td>392</td>
<td>218</td>
<td>2.51</td>
</tr>
<tr>
<td>5</td>
<td>402</td>
<td>240</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Table 2

Pit depth data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of Pits</th>
<th>Maximum Depth (µm)</th>
<th>Median Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>361</td>
<td>361</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>653</td>
<td>449</td>
</tr>
<tr>
<td>3</td>
<td>34</td>
<td>899</td>
<td>621</td>
</tr>
<tr>
<td>4</td>
<td>21</td>
<td>822</td>
<td>681</td>
</tr>
<tr>
<td>5</td>
<td>68</td>
<td>505</td>
<td>363</td>
</tr>
</tbody>
</table>

Fig. 1. Scatterplot of initiation rate versus applied electrochemical potential.

Fig. 2 suggests that initiation rate increases substantially as pH increases from 2.51 to 2.57, then decreases sharply. However, this appearance is due to the fact that the samples with pH = 2.51 and pH = 2.57 differ greatly in the observed initiation rate. It is quite possible that random variation is large, or the initiation rate is influenced by factors not measured. It may not be reasonable to expect a noticeable effect of pH when there is little variation in pH from sample to sample.

Fig. 3 seems to suggest that the initiation rate in-creases sharply with exposure time, then decreases almost to zero when the exposure time becomes large. The extremely low value at 480 does not appear to reflect the effect of exposure time alone, because more pits would have formed in the earlier part of the exposure interval. This low value may be due to the low Eapp value of 372, the high pH of 2.67, to factors not measured, or to random variation. While it is possible that initiation rates vary with time, the data do not provide a reliable estimate of this
variation.

Figs. 1–3 present univariate relationships between environmental factors and initiation rates. They do not capture any interactions that may be present, in which the effect of one factor may depend on the other.

Henshall (1996) pointed out that the data are insufficient to draw many firm conclusions. Henshall suggested that increasing applied electrochemical potential could increase the number of pits per unit area; that appears to be somewhat less certain because of the very different numbers of pits in the two samples with identical values of $E_{\text{app}}$. Another possible explanation is the existence of interactions between pits competing for the same environmental resources.

For each sample the median depth was divided by the exposure time to get an estimate of the average growth rate for that sample. Figs. 4–6 are plots of the estimated rate of increase in median depth against $E_{\text{app}}$, pH, and exposure time, respectively.

Henshall (1996) points out that the effect of electrochemical potential on pit depth is not clear. In addition, it does not seem possible to clearly describe a trend associated with pH. There is evidence that the growth rate decreases with exposure time. Further evidence for this will be presented using a comparison of the median and maximum depths, and by constructing a model in which growth rate is decreasing with time.

In summary, while pit initiation and growth rates are affected by environmental conditions, there is not enough information to model these effects precisely. We will therefore estimate initiation rates separately for each sample. This will illustrate the degree to which the distribution of pit depths can vary under differing environmental conditions, without providing a precise mathematical form for this variation. Growth rates are modeled as decreasing in time.

5. Estimation of rates

Since the number of pits is counted only at the end of the exposure period, there is not enough information to determine how the initiation rate varies with time. For simplicity it is assumed to be constant. Let $\phi$ be the initiation rate for a given sample. This rate does not change as pits are initiated, so the numbers of pits initiated in disjoint time intervals will be independent. The number of pits $n$ then has the Poisson distribution with mean $\phi T$ (Karlin and Taylor, 1975). Given $n$, the initiation times are thus independent and uniformly distributed on the time interval $(0, T)$. The ages of the pits are also independent and uniformly distributed on $(0, T)$.

In the Henshall data, pits with depths less than 25 $\mu$m were not counted. Thus the distribution of the ages of the counted pits is not quite uniform; instead it is skewed somewhat toward the earlier times. This distribution is approximated as uniform on $(0, T)$.

The mean of $n$ is $E(n) = \phi T$. We can therefore estimate $\phi$ with

$$\hat{\phi} = \frac{n}{T} \tag{1}$$

The median depth is well approximated by the mean depth of a pit initiated at the median time, $T/2$. The maximum depth can be approximated with the mean depth of a pit initiated at the beginning of the interval, at $t = 0$. If the growth rate were constant, the maximum depth would be approximately twice the depth of the median. It can be seen in all five samples that the maximum is considerably less than twice the median (Sample 1 gives no useful information because there

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**Fig. 3.** Scatterplot of initiation rate versus exposure time. The two points with equal values of $E_{\text{app}}$ are distinguished.

**Fig. 4.** Scatterplot of growth rate versus applied electrochemical potential.

**Fig. 5.** Scatterplot of growth rate versus pH.

**Fig. 6.** Scatterplot of growth rate versus exposure time.
is only one pit). Therefore it is reasonable to conclude that the growth rate is a decreasing function of the age of the pit. This decrease is taken to be a power of the age, and the mean growth rate is modeled as \( \lambda(t) = \alpha t^{-\beta} \), where \( \alpha > 0 \) and \( \beta > 0 \). This is essentially the model given by Equation (6) in Henshall (1996), except that, since \( \alpha \) is being estimated separately for each sample, it is regarded as fixed rather than random.

The parameters \( \alpha \) and \( \beta \) must now be estimated. This is done by using the fact that the mean depth of a pit at age \( t \) is \( \int_0^t \lambda(u)du \). Let \( d_1, \ldots, d_n \) be the observed depths of the pits. Since the median depth is approximated by the mean depth of a pit aged \( T/2 \), the following estimating equation is used:

\[
\int_0^{T/2} \alpha t^{-\beta} dt = \text{median}(d_i)
\]

The mean maximum depth can be approximated with the mean depth of a pit that initiates at time 0. Intuitively it would seem that this should be a slight overestimate when there are few pits (because the first pit will initiate at a time somewhat greater than 0) and will be a slight underestimate when there are many pits (because the maximum depth will belong to a pit that initiated near time 0 and grew at a rate faster than the others). Simulations show that this is the case. For sample 2, with only six pits, the underestimate appears to be about 10%, for samples 5, with 68 pits, the overestimate appears to be about 5%, and for samples 3 and 4, with 34 and 21 pits, respectively, the error appears to be less than 1%. So this is a reasonably good approximation. Therefore the following estimating equation is used:

\[
\int_0^T \alpha t^{-\beta} dt = \text{maximum}(d_i)
\]

These equations are solved for \( \alpha \) and \( \beta \) for samples 2–5. For sample 1 there is only one pit, and therefore no way to estimate a variation in growth rate. The growth rate for sample 1 is therefore assumed to be constant, with \( \beta = 0 \) and \( \alpha = d/(T/2) = 361/(480/2) = 1.5042 \). Table 3 presents the estimated rates for all five samples.

### 6. Estimating the distribution of the maximum depth

For each sample, 10,000 data sets were generated based on the rates estimated for that sample. The method used was as follows. Let \( T \) be the exposure time, let \( \hat{\phi} \) be the estimated initiation rate and let \( \hat{\lambda}(t) \) be the estimated growth rate, as found in Table 3. For each data set, the number of pits \( n \) was generated from a Poisson distribution with mean \( \hat{\phi}T \). If \( n = 0 \) the data set is discarded. Otherwise, \( n \) pit ages \( t_1, \ldots, t_n \) were then generated from the uniform distribution on \((0, T)\). For each \( t_i \), a depth \( d_i \) was generated from the Poisson distribution with mean \( \hat{\lambda}(t_i) \). For each data set generated in this way, the maximum value of \( d_i \) was recorded. These 10,000 maximum values are a random sample from the distribution of maximum depths.

The distribution of the maximum depth was estimated in two different ways. The first estimate is the empirical distribution of the sample maximum values (this is the parametric bootstrap). Second, a generalized extreme value (GEV) distribution was fit to the set of maxima by maximum likelihood. The GEV distribution is a three-parameter family with parameters \( \xi, \mu, \) and \( \sigma \) whose cumulative distribution function is

\[
F(x) = \exp\left[-\left(1 + \frac{x - \mu}{\sigma}\right)^{-1/\xi}\right]
\]

When \( \xi < 0 \), which turns out to be the case for our data, then the expression above is valid for \( x < \mu - \sigma/\xi \), while \( F(x) = 1 \) for \( x > \mu - \sigma/\xi \). The probability density function for the GEV distribution is

\[
f(x) = \frac{1}{\sigma}\left(1 + \frac{x - \mu}{\sigma}\right)^{-1-1/\xi}\exp\left[-\left(1 + \frac{x - \mu}{\sigma}\right)^{-1/\xi}\right]
\]

for \( x < \mu - \sigma/\xi \), and \( f(x) = 0 \) for \( x > \mu - \sigma/\xi \). The maximum likelihood estimates for \( \xi \) were significantly different from 0 (negative, in fact) for each sample. This suggests that the Gumbel distribution, often used to model the distribution of maximum depths, is not appropriate for these data. The Gumbel distribution is the limit of the GEV distribution as \( \xi \to 0 \).

For each sample, two plots are presented. The first is the histogram of the bootstrap density with the density of the GEV distribution superimposed, and the second is the bootstrap cumulative distribution function with the GEV cumulative distribution function superimposed. The bootstrap and GEV estimates are quite similar, especially for samples 3–5 where the numbers of pits are larger.

Table 4 presents the mean and standard deviation of the maximum depth for each of the five estimated GEV distributions.

The means are all reasonably close to the observed maxima. The standard deviations decrease as the estimated initiation rate, or equivalently, the observed number of pits increases. This reflects the fact that when more pits are observed, the maximum is more likely to be near the mean of its distribution.

The GEV distribution is the asymptotic limit of the maximum of a random sample as the sample size approaches infinity. It is therefore a good approximation when the sample size is reasonably large. In our example the sample size is the number of pits, which varies from quite small to reasonably large.

The goodness-of-fit of the GEV distribution was measured with the one-sample Kolmogorov-Smirnov (KS) distance. For each sample, a second set of 10,000 data sets was generated based on the estimated initiation and growth rates for that sample, as shown in Table 3. This provided a sample of 10,000 maximum depths independent of those used to estimate the parameters of the GEV distribution. The KS distance is the maximum difference between the empirical cumulative distribution function of the 10,000 maximum depths and the GEV cdf. A test of the null hypothesis that this sample of 10,000 maxima came from the fitted GEV distribution was then performed. Although the GEV distributions are close to the empirical distributions, as seen in Figs. 7–14, the null hypothesis was rejected at the 5% level in each case. This is not surprising; the GEV distribution is not exactly the same as the empirical one, and the test has the power to detect even a small difference. Table 5 presents the KS distances. The closeness of the GEV approximations can be seen in the values of the KS distance (see Figs. 15 and 16).

A single GEV distribution was constructed to describe the

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initiation Rate ( \hat{\phi} ) (pits/min)</th>
<th>Growth Rate ( \hat{\lambda}(t) ) (( \mu )min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.002</td>
<td>1.50</td>
</tr>
<tr>
<td>2</td>
<td>0.050</td>
<td>26.64 ± 0.437</td>
</tr>
<tr>
<td>3</td>
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<td>26.26 ± 0.467</td>
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<tr>
<td>4</td>
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<td>51.71 ± 0.726</td>
</tr>
<tr>
<td>5</td>
<td>0.283</td>
<td>17.71 ± 0.526</td>
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</table>

### Table 4

<table>
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<th>Sample</th>
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<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>902.71</td>
<td>29.75</td>
</tr>
<tr>
<td>4</td>
<td>827.90</td>
<td>25.125</td>
</tr>
<tr>
<td>5</td>
<td>524.42</td>
<td>15.353</td>
</tr>
</tbody>
</table>
distribution of the maximum pit depth by combining the results of all five samples. This was done as follows. Each of the five estimated GEV distributions is determined by three parameters ($\mu$, $\sigma$, and $\xi$) estimated by maximum likelihood. The variance of each of these maximum likelihood estimates is also estimated (not shown). For each of the three parameters, the weighted mean of the five estimates was computed, using the reciprocals of the variances as the weights. In this way the estimates with smaller variances are weighted more heavily; in fact this weighting minimizes the variance of the weighted mean. These weighted means are the parameters of the distribution that combines the results of all five samples. Table 6 presents the parameters of this distribution, and Fig. 17 presents the cumulative distribution function.

7. Extrapolating to a future time

The parameter estimates in Table 3 were used to estimate the distribution of the maximum depth for each sample after 500 min of exposure. Again both the parametric bootstrap and the GEV distribution were used. Table 7 presents the median and Table 8 presents the 95th percentile of the distribution of the maximum depth, along with 95% confidence intervals.

![Sample 1](image1.png)

Sample 1 probability density function and cumulative distribution function.

![Sample 2](image2.png)

Sample 2 probability density function and cumulative distribution function.
confidence intervals, based on the GEV distribution. The parametric bootstrap results (not shown) were nearly identical.

To estimate the median and 95th percentile of the distribution of maximum depth, 10,000 data sets were generated based on the estimated initiation and growth rates for each sample, as shown in Table 3, and estimated the median and 95th percentile of the maximum depth with the sample median and 95th percentile of the 10,000 maximum depths. The method used to construct the 95% confidence intervals for the median is described as follows. An analogous method was used for the confidence intervals for the 95th percentile.

For each sample, 1000 additional data sets were generated based on the estimated initiation and growth rates for that sample, as shown in Table 3. For each of these 1000 data sets, estimates of the parameters \( \phi, \alpha, \) and \( \beta \) were computed, based on that data set. Let \( \hat{\phi}_i, \hat{\alpha}_i, \hat{\beta}_i \) be the estimates of the parameters \( \phi, \alpha, \) and \( \beta \) computed from the \( i \)th data set. Let \( m_i \) be the median of the 1000 maximum depths generated from the parameter values \( \hat{\phi}_i, \hat{\alpha}_i, \hat{\beta}_i \) and the maximum depth for each dataset was recorded, thus obtaining a sample of 1000 maximum depths. Let \( m_\text{median} \) be the median of the 1000 maximum depths.

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8. Conclusions

A simple stochastic model has been proposed that can be fit to data consisting of numbers of pits along with the median and maximum depths. The model can be used to estimate the distribution of the maximum depth at longer exposure times and to construct confidence intervals for quantiles of this distribution such as the median and 95th percentile.

The distribution of the maximum is well-described by a Type III extreme value distribution. A Type I, or Gumbel distribution, does not appear to fit as well.

While pit initiation rates varied considerably from sample to sample, the data did not provide enough information to specify this variation as a function of measured physical parameters. Our model estimated a separate homogeneous rate for each sample, and was able to reproduce the maximum depth well.
References


Modeling Pit Growth as a Function of Environmental Variables Through Stochastic Approaches

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Colorado School of Mines, Golden, CO 80401

ABSTRACT

It is well known that rates of pitting corrosion damage are influenced by environmental variables such as applied potential, temperature, and concentrations of ions in solution. Regression methods have been used to estimate the maximum pit depth as a function of environmental parameters. In this paper, regression methods are used both to predict the maximum depth and to estimate the probability distribution of the maximum depth at a future time. It is shown that these predictions can be reasonably accurate (within 15% of the true value) even when the true mathematical relationships between pitting rates and environmental parameters are nonlinear, and in some circumstances when future values of the environmental variables are not known.

Introduction

The interim dry storage disposal of commercial used nuclear fuel consists of fuel assemblies either from pressurized water reactor (PWR) or boiling water reactor (BWR) fitted into 8 m 3 canisters fabricated from 304 and 316 austenitic stainless steels surrounded by overpack concrete, for an as-yet unspecified period above ground, probably several decades, followed by transfer to geological disposal facilities for permanent housing upon availability. The 62 (as of 2011) independent spent fuel storage installations (ISFSI) that currently exist in the US, associated with operating reactors or shutdown reactors sites, are located in both coastal and rural areas, with total of about 2000 loaded dry storage casks. The outer surfaces of canisters housed in concrete overpack will are likely to be exposed to chloride-bearing particulates from sea-salt aerosol and/or industrial pollution through the ventilation gap between the outer surface of the canister and the inner surface of the concrete overpack, and susceptible to stress corrosion cracking under existing tensile stress. Estimating the lifetime of dry storage canisters requires the ability to correctly predict and monitor materials degradation so that corrective maintenance actions can be taken in an appropriate time frame. Chloride-initiated stress corrosion cracking (CISCC) of spent fuel canisters (primarily in welds or heat affected zones) is one of the safety concerns during the dry storage of used nuclear fuel at ISFSI sites.

Deterioration by chloride SCC can lead to canister penetration, potentially releasing helium and radioactive gases, and permitting air ingress which could pose a threat to fuel rod integrity. Quantitative assessments through statistical approaches are already widely used and applied to localized corrosion. Therefore the early stage of pitting growth rate is required to be able to determine the lifetime performance of canisters at various sites, and prediction of the remaining life of the canister.


The Generalized Extreme Value (GEV) family of distributions is the only possible limit distribution for the maximum of independent and identically distributed random variables (Coles, 2001) 27. The Extreme Value (EV) family is a subfamily of the GEV family obtained by setting a shape parameter equal to zero. The GEV and EV families have often been used to model maximum pit depth: see, for example, Kowaka, (1994) 28, Melchers, (2008), Valor, et al., (2013) 29, Benstock and Cegla (2015) 18. In most cases, extreme value methods have been used to estimate the maximum depth at the time of the analysis rather than to predict the maximum, or its probability distribution.

This paper addresses the ability to extrapolate pit growth rate as a function of environmental variables using both regression and extreme value (EV)
approaches. The economically important application of extrapolation of the corrosion rate is to determine a time frame of canister inspection of dry storage cask and crack repair if required. Several challenges arise in the prediction of canister lifetime. First, there are many variables reflecting environmental, stress, and material properties affecting the lifetime. Second, the relationships between those variables and canister lifetimes may be difficult to model precisely. Finally, information about them and interactions and other relationships between the variables is often difficult to obtain.

The simulations presented are based on a model of Henshall (1992) in which pitting parameters are specified as a function of environmental variables, which vary over time. The simulations illustrate how regression methods may be used for future predictions, both of the maximum depth itself and of the probability distribution of maximum depth. Specifically, the accuracy of a linear model is explored in situations where the true model is not linear.

The simulated pit depths are produced by a nonlinear model of applied potential ($E_{app}$), chloride ion concentration ($Cl$), and absolute temperature ($T$). Two models are fitted and extrapolated to predict the future maximum depth. In the first, the maximum depth is modeled as a log linear function of time and environmental variables. In the second, the parameters of an extreme value (EV) distribution are modeled as a log linear function of time and environmental variables, and extrapolated to estimate the parameters of the distribution at a future time. For each model, two situations are considered: In the first, the environmental parameters follow a deterministic function of time in which the future values are known, and in the second, the variables follow a stochastic process in which the future values are not known.

### Simulation Methods

#### Environmental Parameters

Two models for the variation over time of the environmental variables $E_{app}$, $Cl$, and $T$ are considered. In the first, these variables varied with time in a deterministic fashion as follows:

$$E_{app} = 1.4 - \exp(-0.047t)$$  

Equations (1) and (3) are identical to those in Henshall (1992). Henshall modeled $Cl$ concentration as increasing exponentially in time. Here it is modeled as a sine wave, which simulates dry and wet cycles of $Cl$ concentration, as observed in data measured from various meteorological stations at ISFSI sites. Equation (1) represents an increase in corrosion potential toward the asymptotic limit as suggested by Macdonald and Urquiddi (1990). Equation (3) simulates exponential decay heat due to fission products decay.

In the second model, the values for temperature were deterministic as in the first model, while $E_{app}$ and $Cl$ were modeled as autoregressive processes. The value of $T$ was made deterministic because it seemed reasonable to assume that it would decrease rather than fluctuate randomly. The means and standard deviations were taken to be the same as those in the deterministic model. The distribution was taken to be normal, with the correlation between the value at time $t$ and the value at time $t + 1$ taken to be 0.5, and the values constrained to be positive.

#### Pitting Parameters

Three pitting parameters were specified: the initiation rate $\lambda$, the death rate $\tau$, and the growth rate $\gamma$. These parameters are given by the following functions of the environmental variables $E_{app}$, $Cl$, and $T$.

$$\lambda = A_1(E_{app} - B_1) \exp(C_1 Cl) \exp(-Q_1 / RT)$$  

$$\tau = A_2 \exp(-C_2 Cl) \exp(-Q_2 / RT)$$  

$$\gamma = A_3(E_{app} - B_3) C_3 \exp(Q_3 / RT)$$  

where $A_1 = 1.541 \times 10^{12}$, $A_2 = 0.0971$, $A_3 = 9.5 \times 10^{-8}$, $B_1 = 0.4$, $B_2 = 0.4$, $B_3 = 0.3$, $C_1 = 1.0$, $C_2 = 0.2$, $Q_1 = 2.27 \times 10^3$, $Q_2 = 1600$, $Q_3 = 10^4$, and $R = 1.9858$.

Equations (4)–(6) are based on models in Henshall (1992). Henshall chose values for the
values of some constants vary to provide reasonable values for $\lambda$, $\tau$, and $\gamma$ over the range $0 < t \leq 150$. The values of some constants were modified so as to provide reasonable values for all $t \leq 200$. The environmental variables $E_{\text{app}}$, $C_l$, and $T$ vary with time, so the pitting parameters do as well. Figure 1 presents plots of the values of the pitting parameters, versus time, for the deterministic model.

Our models do not take into account possible long-term variations in the pitting mechanism that can affect the rate of pit growth, such as the limitation on cathodic current available to a pit, which implies a potential limit to pit depth. See, for example Chen et al., (2008)\textsuperscript{28}, Chen and Kelly (2010)\textsuperscript{29}.

![Figure 1: Values of the pitting parameters over time.](image)

Simulation Methods
The data were simulated as follows: A coupon divided into 1000 regions was considered. At each time step, each region that did not contain a pit had a pit initiated with probability $\lambda$. Then for each region that contained a pit, the pit depth increased by one unit with probability $\gamma$ and repassivated with probability $\tau$. The simulation was run for 200 time steps.

Twenty coupons were simulated, and recorded the maximum depth for each coupon at 20 evenly spaced times $t_1 = 6$, ..., $t_{20} = 120$. The values of the environmental variables were taken to be the same for each coupon.

Prediction Methods
Accurate prediction of the lifetime of a canister is strongly dependent on the ability to predict the maximum depth of the pits. Following are descriptions of and comparisons between two methods, one based on linear regression and one based on fitting an extreme value (EV) distribution.

Predicting the Maximum Depth
For the simulations where the values of the environmental variables were deterministic, it was assumed that their values for $t > 120$ were known at $t = 120$.

Let $\text{max}_j(t)$ denote the maximum depth for coupon $j$ at time $t$. Let $\overline{E}_{\text{app}}(t)$, $\overline{C}_l(t)$, and $\overline{T}(t)$ denote the mean values of $E_{\text{app}}$, $C_l$, and $T$ over the interval $(0,t)$. Equation (7) presents the model, and Equation (8) presents the predicted value of the maximum at $t = 200$. Our simulations extrapolate from $t=120$ to $t=200$ time units, which should be short enough for these long-term variations not to have a significant impact. If the conditions specified by these equations are not approximately met, the regression and EV approaches described here may still work well if environmental variation and the pitting mechanism can be adequately described in equations that would replace (1) through (6).
\[
\ln \max_f(t_i) = \beta_0 + \beta_1 \ln \bar{E}_{app}(t_i) + \beta_2 \ln \bar{C}(t_i) + \beta_3 \ln \bar{T}(t_i) + \beta_4 \ln t_i
\] (7)

\[
\max(200) = \exp(\beta_0 + \beta_1 \ln \bar{E}_{app}(200) + \beta_2 \ln \bar{C}(200) + \beta_3 \ln \bar{T}(200) + \beta_4 \ln 200)
\] (8)

For the simulations where \( E_{app} \) and \( Cl \) were generated at random, their values for \( t > 120 \) were assumed not to be known at \( t = 120 \). For these simulations the mean values at \( t = 200 \) were estimated with the mean values at \( t = 120 \). The predicted value of the maximum depth at \( t = 200 \) is

\[
\max(200) = \exp(\beta_0 + \beta_1 \ln \bar{E}_{app}(120) + \beta_2 \ln \bar{C}(120) + \beta_3 \ln \bar{T}(200) + \beta_4 \ln 200)
\] (9)

The linear model given by equation (7) predicts the value of \( \ln \max_f(t_i) \). Level 95% prediction intervals were computed for the log of the maximum depth (see, e.g. Devore, 2016) and exponentiated to obtain 95% prediction intervals for \( \max(200) \).

### Predicting the Distribution of the Maximum Depth

The distribution of the maximum depth was estimated with an extreme value (EV) distribution. The EV distribution is a special case of the generalized extreme value (GEV) distribution. The GEV distribution has three parameters, a location parameter \( \mu \), a scale parameter \( \sigma \), and a shape parameter \( \xi \). The EV distribution is obtained by setting \( \xi = 0 \). The EV distribution fit our data well, so it was preferred for its relative simplicity. The cumulative distribution function of the EV distribution is

\[
f(x) = \frac{1}{\sigma} \exp\left(-\frac{x - \mu}{\sigma}\right) \exp\left(-\exp\left(-\frac{x - \mu}{\sigma}\right)\right)
\]

It was assumed that the maximum depth at time \( t_i \) followed the EV distribution with parameters \( \mu(t_i) \) and \( \sigma(t_i) \). For each \( t_i \), \( \mu(t_i) \) and \( \sigma(t_i) \) were estimated by maximum likelihood, obtaining estimates \( \hat{\mu}(t_i) \) and \( \hat{\sigma}(t_i) \). A model was then fit for each of these parameters. For \( \mu \) the model was

\[
\ln \mu(t_i) = \beta_0 + \beta_1 \ln \bar{E}_{app}(t_i) + \beta_2 \ln \bar{C}(t_i) + \beta_3 \ln \bar{T}(t_i) + \beta_4 \ln t_i
\] (10)

with a similar model for \( \sigma \).

The parameters \( \mu(200) \) and \( \sigma(200) \) were then estimated using the estimates obtained. So \( \mu(200) \) was estimated with

\[
\hat{\mu}(200) = \exp(\hat{\beta}_0 + \hat{\beta}_1 \ln \bar{E}_{app}(120) + \hat{\beta}_2 \ln \bar{C}(120) + \hat{\beta}_3 \ln \bar{T}(200) + \hat{\beta}_4 \ln 200)
\] (11)

with a similar model for \( \sigma \). For models where \( E_{app} \) and \( Cl \) were generated at random, equation (11) was used, with \( \bar{E}_{app}(200) \) and \( \bar{C}(200) \) replaced by their values at \( t = 120 \). A limited sensitivity study was performed by changing the values of the environmental variables \( E_{app} \) and \( Cl \) in equations (9) and (11).
by ±15%. It is assumed these values are subjected to higher uncertainty than the temperature variation at canister surface, since the computational methodology of canister surface temperature is well established.

**Results**

Results were obtained for both deterministic and random environmental parameters. Simulations were performed using MATLAB (Version 7.10.0, Release 2010a). Predicted values for the maximum depth and its distribution were obtained using the procedures described in the previous section.

**Predicting the Maximum Depth for Deterministic Variables**

Figure 2 presents results for deterministic values of the environmental parameters, following Equations (1)–(3). Depths were measured at 20 times: \( t = 6, 12, ..., 120 \).

![Figure 2](image)

Figure 2. 95% prediction intervals for the maximum depth at \( t = 200 \); environmental parameters deterministic. The histograms on the left of each plot represent the distributions of maximum depth at \( t = 120 \), while the histograms on the right represent the distributions of maximum depth at \( t = 200 \). (a) Approximation using lower limit for environmental variables. (b) Approximation using estimated values for environmental variables. (c) Approximation using upper limit for environmental variables.

The histograms are the same in each plot. The histogram on the left is the distribution of maximum depths of 1000 coupons at time \( t = 120 \), and the histogram on the right is the distribution of maximum depths for 1000 coupons at time \( t = 200 \). These histograms provide approximations to the true distributions of maximum depth at these times. The intervals represent the 95% prediction intervals for the maximum depth at \( t = 200 \), and the "x" represents the point estimate of the maximum depth. A total of 1000 prediction intervals were generated from samples of 20 coupons. Figure 2(a) presents the interval based on the lower limit of the environmental variables, Figure 2(b) presents the interval based on the estimated values for the environmental variables, and Figure 2(c) presents the interval based on the upper limit of the environmental variables. The estimator is nearly unbiased. The true mean at \( t = 200 \) was 105.13, and the mean of 1000 estimates was 105.11, with a standard deviation of 4.93. The prediction interval is not very sensitive to the values of the environmental variables. The intervals for environmental variables at the lower and upper limits are not much different than those computed using the original values.
Predicting the Maximum Depth for Random Variables

Figure 3 presents results for random values of $E_{app}$ and Cl. Depths were measured at 20 times: $t = 6, 12, ..., 120$.

![Histograms](image)

Figure 3. 95% prediction intervals for the maximum depth at $t = 200$; $E_{app}$ and Cl generated randomly. The histograms on the left of each plot represent the distributions of maximum depth at $t = 120$, while the histograms on the right represent the distributions of maximum depth at $t=200$. (a) Approximation using lower limit for environmental variables. (b) Approximation using estimated values for environmental variables. (c) Approximation using upper limit for environmental variables.

The model did not predict as well for data generated by random environmental variables as for deterministic ones. The estimator has a bias of about 11%. The true mean at $t = 200$ was 105.53 and the mean of the 1000 estimators was 92.88 with a standard deviation of 1.69. The prediction intervals for randomly generated environmental variables is more sensitive to the values of those variables than the intervals for deterministic variables. Still, the intervals calculated from the lower and upper limits do contain the true distribution between them.

Predicting the Distribution of Maximum Depth for Deterministic Variables

Figure 4 presents results for deterministic values of the environmental parameters, following Equations (1)–(3). Depths were measured at 20 times: $t = 6, 12, ..., 120$. 

Figure 4. EV approximations to the distribution of the maximum depth at $t = 200$; environmental parameters deterministic. The histograms on the left of each plot represent the distributions of maximum depth at $t = 120$, while the histograms on the right represent the distributions of maximum depth at $t = 200$. (a) Approximation using lower limit for environmental variables. (b) Approximation using estimated values for environmental variables. (c) Approximation using upper limit for environmental variables.

Table 1 presents the estimated values of the EV parameters for Figure 4.

<table>
<thead>
<tr>
<th>Figure</th>
<th>$\mu$</th>
<th>$\sigma$</th>
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<tbody>
<tr>
<td>4a</td>
<td>101.61</td>
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</tr>
<tr>
<td>4b</td>
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<td>0.73</td>
</tr>
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<td>4c</td>
<td>111.23</td>
<td>1.53</td>
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</table>

The histograms are the same as those in Figures 2 and 3. They provide approximations to the true distributions of maximum depth at $t = 120$ and $t = 200$. The curves represent the EV approximation to the distribution of maximum depths at $t = 200$. A total of 1000 curves were generated from samples of 20 coupons. Figure 4(a) presents the interval based on the lower limit of the environmental variables, Figure 4(b) presents the interval based on the estimated values for the environmental variables, and Figure 4(c) presents the interval based on the upper limit of the environmental variables.

The EV distribution provides a good approximation to the true distribution on the average. The average of the means of the 1000 distributions was 105.58, which is very close to the true mean of 105.13. The spread of the distribution was also well estimated. The average of the standard deviations was 2.65, while the standard deviation of the true distribution was 2.43. As with the prediction intervals, the extreme value distributions are not very sensitive to the values of the environmental variables.

Predicting the Distribution of Maximum Depth for Random Variables

Figure 5 presents results for random values of $E_{\text{app}}$ and $C_l$. Depths were measured at 20 times: $t = 6, 12, ..., 120$. 
Table 1 presents the estimated values of the EV parameters for Figure 4.

Table 2: EV Parameters for Figure 5

<table>
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<tr>
<th>Figure</th>
<th>( \mu )</th>
<th>( \sigma )</th>
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<tbody>
<tr>
<td>Figure 5a</td>
<td>68.43</td>
<td>1.90</td>
</tr>
<tr>
<td>Figure 5b</td>
<td>93.51</td>
<td>2.80</td>
</tr>
<tr>
<td>Figure 5c</td>
<td>122.54</td>
<td>5.31</td>
</tr>
</tbody>
</table>

The model did not predict as well for data generated by random environmental variables as for deterministic ones. The average of the means of the distributions was 91.89, and the true mean was 105.53, for a bias of about 13%. The spread of the distribution was well estimated, however. The average of the standard deviations was 2.67, while the standard deviation of the true distribution was 2.43. As with the prediction intervals, the extreme value distributions were more sensitive to the values of the environmental variables than in the deterministic case. Still, the intervals calculated from the lower and upper limits do contain the true distribution between them.

The following linear model was also fit to both the deterministic and random data. This model performed better than the log linear model for the random environmental variables but less well for the deterministic variables. Models with the final observation at \( t = 100 \) rather than \( t = 120 \) were also fit. In general, model performance varied between deterministic and random environmental variables, between linear and log linear models, and with the value of the final observation. In all situations the mean value of the estimator was within 15% of the true mean.

Feasibility of Choosing a Model

The success of an extrapolation depends in part on how well the past measured environmental data represents future values. In laboratory experiments where values of environmental variables are controlled, the distribution of pit depths follows a stochastic process, and future pit depths are then
predicted by extrapolating the process. This is not the case when a canister is subjected to the ambient environment in the field, which is impossible to replicate in a laboratory setting. The results reported here are for log linear models, but, as mentioned above, linear models were also fit. Simulations were performed to determine how feasible it might be to choose between models for extrapolation based on the fit to existing data. Both linear and log linear models were fit to deterministic data for \( t \leq 120 \). Both models fit the data for \( t \leq 120 \) well, but varied in the accuracy of extrapolation. Figure 6 presents the observed maxima for the deterministic environmental variables at values of \( t \) (solid line), estimated values at \( t = 6, \ldots, 120 \) (dots) from the log linear model (left) and linear model (right). The dashed line represents the extrapolated estimates for \( t > 120 \). Both models fit the observed data \( t \leq 120 \) very well. However, the extrapolated values for the log linear model are noticeably more accurate than those from the linear model. It would seem difficult to predict which model would extrapolate more accurately based on information available at \( t = 120 \).

In our deterministic model, it was assumed that future values of environmental variables were known. For the random model, future values were not assumed known, but they were generated by a process that assured that the means would be constant over time. In a situation where future values are not known, and the mean values vary over time, it may be difficult to extrapolate reliably.

**Conclusions**

The data simulated in this study are based on an estimated relationship between the pitting parameters and three main environmental parameters: \( E_{app} \), Cl, and temperature. Strictly speaking, our conclusions are therefore limited only to the situation described in equations (1) through (6). However, it is reasonable to believe that they may also be valid more generally where these equations approximate the relationship between pitting parameters and environmental variables. No simple model describes the relationship between environmental variables and maximum depth exactly. In general, a linear or log linear model will fit the observed values quite well. The accuracy of an extrapolation to a future time depends on how similar the relationship between parameters and depths in the future is to the relationship in the past. This is dependent on the type of model that is
fit, on the future values of the environmental variables, and on how far in the future one is extrapolating. There does not appear to be an easy way to determine which model will lead to the most accurate extrapolation. However, our results suggest that both linear and log-linear models fit reasonably well, with errors of less than 15% on the average.

References
3. Padovani, C., Albores-Silva, O. & Charles, A. Corrosion control of stainless steels in indoor atmospheres laboratory measurements under MgCl2 deposits at constant
Construction and Application of a Likelihood Function for Pit Growth Rates with Confidence Bounds

<table>
<thead>
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</table>
Construction and Application of a Likelihood Function for Pit Growth Rates with Confidence Bounds

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aDepartment of Applied Mathematics and Statistics, bDepartment of Physics, Colorado School of Mines, Golden, CO 80401

Abstract

A new flexible stochastic methodology is presented to simulate of pit initiation, growth rate, and death to predict maximum pit depth at a future time. When applied to experimental data, the model fits the data very well, and estimates of the maximum pit at future times are reasonably accurate. Specifically, the construction of a nominal 95% prediction interval that covers the future maximum depth with high probability, even after accounting for measurement error.

1 Introduction

Pitting corrosion evaluation forecasts are tightly integrated into our routine design, operational system, and maintenance for all metallic structures. There are two main components of pitting corrosion measurements, one based on actual field structures and the other on laboratory experiments under controlled environments, and the relation between them is not straightforward. These experimental data sets are central to all mathematical models describing corrosion processes affecting structures. The lack of accuracy of corrosion forecasts can stem from two main types of factors. The first is built-in uncertainty in the environment, material properties, and manufacturing process. For example, small changes in environmental parameters can make a very large impact on pit growth rates and projections of the structure lifetime. The second factor that puts uncertainty into the forecast of corrosion process is inaccuracies in the measurements themselves and in mathematical models. The lack of accuracy can be caused by errors in the measurement devices or by a shortage of measurement data, while the accuracy of the mathematical model is usually limited by the inability to fully represent the physical processes of corrosion, such as electrochemical interaction within the pit’s depth, and between neighboring pits. There is a tremendous value for humanity in improving the quality of corrosion process prediction. Early prediction of the corrosion propagation rate can save human life and have significant economic cost benefits. In addition, it can contribute to the effectiveness of lifetime design systems, and optimum maintenance schedules.
Pitting corrosion, which may lead to stress corrosion cracking (SCC), are, like many other phenomena where environmental factors involved, complex in nature and therefore require the coupling of several mathematical models and sub-models in order to describe and analyze SCC. The coupling models used for the analysis of corrosion can broadly be classified into three following categories: (1) Existence of an aggressive environment. The stochastic models used for the environmental parameters are based on observable environmental data such as temperature, relative humidity, pH, and aggressive ion distributions on the metallic surface, such as chlorine, and these parameters are fluctuated randomly. (2) Metal properties not known exactly, such as micro and macro structure, heat history and treatment, surface conditions and their strong interactions with environment (3) Uncertainty in the residual stress analysis, due to lack of information on manufacturing processes (rolling, welding, heat affected zone, HAZ, etc.). These three factors interact with each other, since the output of one model is normally used as input to other models as is shown in Figure 1. Understanding feedback from different models may lead to overall improvement in our prediction of corrosion process methodology. Furthermore, different experimental data sets are generally utilized for the calibration and validation of specific proposed models for that experiment’s data sets. This makes it particularly difficult and computationally complicated to integrate or combine the various physics-based models and stochastic behavior from various experimental data sets into the overall general SCC prediction scheme. The observation indicates that some of them change randomly. In the past various stochastic and physics-based models\cite{1-20} have been used for predicting pitting corrosion and estimating aging of the structure. The Generalized Extreme Value (GEV) and Extreme Value (EV) distribution function families also have been utilized to model maximum pit depth\cite{21-25}. In this paper we are presenting an enhanced robust stochastic model for predicting maximum pit depth and growth rate, accounting for uncertainties which can arise from different sources. We are proposing frameworks that overcome lack of or imprecise information on pit distribution depth and growth rates, and still reproduce meaningful predictive results. The proposed statistical framework method is applied to the laboratory pitting corrosion data generated by Ohio State University and described in reference 26.
The results of this study will provide a basis for possible solutions for effective aging management of metallic structure with quantified uncertainty which is particularly valid for Chlorine Induce Stress Corrosion Cracking (CISCC) cases. As an example, cases for applications to the dry storage canisters holding used nuclear fuel that may be exposed to CISCC, with the possibility of canister confinement failure which causes safety concerns and environmental consequences is given in references 27 through 30.

This paper is structured as follows: Section 2 presents the theoretical background constructing the likelihood function. In Section 3 a short overview of the experimental pitting corrosion data conducted at Ohio State University (OSU) is outlined. Section 4 presents results of applications of likelihood function to the laboratory experimental pitting data. In Section 5 sensitivity and uncertainty methodology with application to the OSU data is presented. In Section 6 conclusions are drawn.

## 2 Description of the Model

The experiments data indicates that the initiation rate is proportional to the proportion of surface that is un-pitted. It follows that the rate is a function of time of the form

\[ r(t) = \gamma e^{-\gamma t} \]  

(1)

Where \( \gamma \) in this study is constant, but it may vary as a function of time.
Let $T$ be the current time. The probability density function (pdf) of the initiation time of a pit existing at time $T$ is given by

$$q(t) = \frac{r(t)}{\int_0^T r(t) \, dt} = \frac{\delta e^{-\gamma t}}{1 - e^{-\gamma T}}$$  \hspace{1cm} (2)$$

We modeled the age at repassivation (death) of a pit as exponentially distributed with constant rate $\delta$. The pdf of the time $s$ of death, for a pit initiated at time $t < s$, is $g(s) = \delta e^{-\delta(s-t)}$. The probability that a pit initiated at time $t$ is still alive at time $T > t$ is $P(s > T) + e^{-\delta(T-t)}$.

We modeled pit growth as a heterogeneous Poisson process with rate $\lambda(t) = at^{b}$, where $t$ is the age of the pit and $0 < b < 1$. The expected depth of a pit at time $T$, given that the pit initiated at time $t$, and is still alive at time $T$, is $\Lambda(T) = \int_t^T \lambda(u) \, du = \frac{a(T-t)^{1-b}}{1-b}$, we reparametrize this as $\Lambda(T) = \alpha (T-t)^{\beta}$, where $0 < \beta < 1$. The probability that a pit has depth $d$ at time $T$, given that it is alive at time $T$, is given by

$$p(d \mid \text{alive at } T) = \exp(\alpha(T-t)^{\beta}) \frac{\alpha(T-t)^{\beta} d^{d}}{d!}$$  \hspace{1cm} (3)$$

The probability that a pit has depth $d$ at time $T$, given that its time of death was $s < T$, is given by

$$p(d \mid \text{dead at } s < T) = \exp(\alpha(s-t)^{\beta}) \frac{\alpha(s-t)^{\beta} d^{d}}{d!}$$  \hspace{1cm} (4)$$

Let $d$ be the depth of a pit at time $T$. Let $t$ be the initiation time and $s$ be the time of death. For $s < T$, the joint probability distribution of $d$, $s$, and $t$ is

$$p(d, s, t) = \exp(\alpha(s-t)^{\beta}) \frac{\alpha(s-t)^{\beta} d^{d}}{d!} \frac{\gamma e^{-\gamma t}}{1 - e^{-\gamma t}} \delta e^{-\delta(s-t)}$$  \hspace{1cm} (5)$$

For $s > T$, the pit is alive at time $T$, so the value of $s$ is unobserved. The pdf of $s$ is replaced with $P(s > T)$ to obtain the joint probability distribution of $d$ and $t$ as follows:

$$p(d, t) = \exp(\alpha(T-t)^{\beta}) \frac{\alpha(T-t)^{\beta} d^{d}}{d!} \frac{\gamma e^{-\gamma t}}{1 - e^{-\gamma t}} e^{-\delta(T-t)}$$  \hspace{1cm} (6)$$

The probability that a pit had depth $d$ at time $T$ is
Let $T_1, \ldots, T_k$ be times at which depths are measured. Let $n_i$ be the number of pits at time $T_i$ and let $d_{i1}, \ldots, d_{in_i}$ be the depths of these pits. The likelihood function for the parameters $\alpha, \beta, \gamma$, and $\delta$ is given by

$$ L(\alpha, \beta, \gamma, \delta; d) = \prod_{i=1}^{k} \prod_{j=1}^{n_i} P(d_{ij}; \alpha, \beta, \gamma, \delta, T_i) $$

(8)

3 Description of the Data

To verify the stochastic model described above the experimental data that was generated at The Ohio State University\(^{26,31}\) is implemented. The data we considered consisted of coarse ground type 304 stainless steel samples exposed up to one year to sea salt particles of a brine (300 $\mu$g/cm$^2$ NaCl) at relative humidities of 40% and 75%, for periods of one week, two weeks, four weeks (1 month), 26 weeks (6 months), and 52 weeks (12 months). Depths of pits with that were greater than 10 $\mu$m were recorded.

Table 1 presents the number of pits and the maximum depth at 1 week, 2 weeks, 1 month, 6 months, and 12 months for 40% RH and 75% RH. Figures 2 and 3 present histograms of the depths of the pits at each time.

**Table 1: Number and maximum depth of pits**

<table>
<thead>
<tr>
<th></th>
<th>40% RH</th>
<th></th>
<th>75% RH</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of pits</td>
<td>Maximum depth</td>
<td>Number of pits</td>
<td>Maximum depth</td>
</tr>
<tr>
<td>1 week</td>
<td>82</td>
<td>31</td>
<td>3</td>
<td>26</td>
</tr>
<tr>
<td>2 weeks</td>
<td>214</td>
<td>33</td>
<td>14</td>
<td>41</td>
</tr>
<tr>
<td>1 month</td>
<td>340</td>
<td>37</td>
<td>17</td>
<td>39</td>
</tr>
<tr>
<td>6 months</td>
<td>1112</td>
<td>63</td>
<td>111</td>
<td>57</td>
</tr>
<tr>
<td>12 months</td>
<td>1408</td>
<td>62</td>
<td>184</td>
<td>64</td>
</tr>
</tbody>
</table>
Our goal was to develop a model to predict the maximum pit depth at 12 months from the depths of the pits at earlier times. An excellent fit was obtained using the data from 1 month and 6 months, as it is shown in Figure 3, so we chose to base our predictions for one year on those two observations.

4 Results

4.1 Likelihood-Based Estimates

We estimated the combination of parameters $\alpha$, $\beta$, $\gamma$, and $\delta$ for both the 40% RH and 75% RH data. Because information about $\gamma$ is contained in the number of pits, we used the number of pits at one month and at six months to estimate $\gamma$, as follows:

Let $n_1$ be the number of pits at one month and let $n_6$ be the number of pits at six months. Let $N$ be a parameter representing the limiting number of pits. Then $n_1$ and $n_6$ both have Poisson distributions with means $E(n_1) = N(1 - e^{-\gamma})$ and $E(n_6) = N(1 - e^{-6\gamma})$. The maximum likelihood estimators $\hat{\gamma}$ and $\hat{N}$ can be found by setting the means equal to the observed values of $n_1$ and $n_6$ and solving.
The experimental data indicated that for 75% RH data, the average initiation rate per month was slightly increased (by about 9%) in the first six months than it was in the first month (17 pits during the first month, \(111/6 = 18.5\) average number pits per month during the first six months). Since it is unlikely to model the initiation rate as increasing in time, we estimated \(\gamma\) with \(\hat{\gamma} = 0\) for the 75% RH data, thus assuming a constant initiation rate. The limiting number \(N\) of pits is then infinite.

To compute estimators of \(\alpha, \beta,\) and \(\delta,\) we substituted for \(\hat{\gamma}\) and maximized equation (8) over \(\alpha, \beta,\) and \(\delta,\) using times \(T_1 = 1\) and \(T_2 = 6\) months. We used the estimates \(\hat{\alpha}, \hat{\beta},\) and \(\hat{\delta}\) to estimate the distribution of pit depths at \(T = 12\) months by using equation (7) to estimate the probability \(\hat{P}(D = d)\) for positive integers \(d.\) The estimated cumulative distribution function (cdf) is \(\hat{P}(D \leq d)\).

In the actual data, depths of 10\(\mu\text{m}\) or less were not included in the measurements. We therefore set the probabilities \(\hat{P}(D = d) = 0\) for \(d < 10\) and rescaled so that the sum of the remaining probabilities would be 1.

Figures 4 and 5 presents plots of the estimated cdf for \(T = 1, \ T = 6\) and \(T = 12,\) The empirical cdf is superimposed. At 40% RH, the fits are very close for both \(T = 1\) and \(T = 6.\) At 75% RH, the fit is close for \(T = 6,\) but less good for \(T = 1,\) where there are only 17 pits. In both cases, the fit when extrapolated to 12 months is very good.

Figure 4: Empirical (solid line) and estimated (dashed line) cdfs of pit depths at 40% RH. Left: 1 month. Center: 6 months. Right: 12 months.
Figure 5: Empirical (solid line) and estimated (dashed line) cdfs of pit depths at 75% RH. Left: 1 month. Center: 6 months. Right: 12 months.

To estimate the maximum depth at \( T = 12 \), we first estimated the number of pits at that time. For the 40% RH data, we estimated the number of pits at \( T = 12 \) as \( \hat{n}_{12} = \hat{N}(1 - e^{-12/\gamma}) \). As oppose for the 45% RH in 75% RH data, the experiments indicated slightly growth in number of pits 111x (1.09)^{12} = 186, assuming constant growth rate of 9%, the estimation is very closed measured number of pits (184, see table 1). We then estimated the maximum depth at 12 months using two different methods. The first method was based on the quantiles of the cdf. Specifically, we estimated the maximum depth \( \hat{m} \) at 12 months as the \( \frac{n_{12}}{n_{12} + 1} \) quantile of the estimated cdf, so

\[
\hat{m} = \text{smallest value of } d \text{ such that } \hat{P}(D \leq d) \geq \frac{n_{12}}{n_{12} + 1}
\]  

(9)

Given that there are \( \hat{n}_{12} \) pits, the cdf of the maximum is given by \( P(m \leq d) = P(D \leq d)^{\hat{n}_{12}} \). The second method is to estimate the maximum with the mean of this cdf.

Let \( m \) be the maximum depth at 12 months. A 95% prediction interval for \( m \) is based on the fact that \( P(m \leq d) = P(D \leq d)^{\hat{n}_{12}} \). A 95% prediction confidence interval is therefore \( (m_L, m_U) \) where

\[
\hat{P}(D \leq m_L) = 0.025\frac{1}{\hat{n}_{12}} \quad \hat{P}(D \leq m_U) = 0.975\frac{1}{\hat{n}_{12}}
\]  

(10)

Table 2 presents the calculations results with confidence bound interval.

<table>
<thead>
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<th>Table 2: Results for ( T = 12 ) months</th>
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<tbody>
<tr>
<td>( \alpha^* )</td>
</tr>
<tr>
<td>( \beta^* )</td>
</tr>
<tr>
<td>( \gamma^* )</td>
</tr>
<tr>
<td>( \delta^* )</td>
</tr>
<tr>
<td>True maximum</td>
</tr>
<tr>
<td>Estimated maximum (quantile)</td>
</tr>
<tr>
<td>Estimated maximum (mean)</td>
</tr>
<tr>
<td>95% Prediction interval</td>
</tr>
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</table>


The maximum pit is somewhat underestimated at 40% RH by about 9%. The quantile method slightly underestimates the maximum pits at 75% RH only by 5%. These estimations are very good taken into consideration of all uncertainties associates with measurements assuming in the ranges of 10%-15%. The mean method estimates it correctly to the nearest µm. In both cases, the true value is contained in the 95% prediction interval. The prediction interval is wider for the 75% RH because there are fewer pits.

### 4.2 Bootstrap Methods

We investigated the accuracy of the estimated maximum and prediction interval with the bootstrap. Using the estimates \( \hat{\alpha} \), \( \hat{\beta} \), \( \hat{\gamma} \), and \( \hat{\delta} \), we computed the estimated cdfs of pit depth at 1 month, 6 months, and 12 months. We then generated 1000 simulated samples at 1 month, 6 months, and 12 months from these cdfs. For the pits at 1 month and 6 months, we multiplied each depth by a random value uniformly distributed between 0.85 and 1.15 to represent measurement error. Sample sizes for 1 month and 6 months were generated from Poisson distributions with means equal to the numbers of pits in the actual samples (340 at 1 month, 1112 at 6 months). The sample sizes at 12 months were generated from a Poisson distribution with mean \( \hat{m} = 1347 \), estimated as described above from the real data. For each simulated sample, we computed estimates \( \hat{\alpha}^*, \hat{\beta}^*, \hat{\gamma}^* \), and \( \hat{\delta}^* \), then estimated the maximum at 12 months, along with a 95% prediction interval, using the same method used for the real data.

Figure 6 presents histograms of simulated maximum depths from 1000 bootstrap samples for both 40% and 75% RH. The distribution is more condensed for 40% RH, because the number of pits were larger. The true maxima are within the middle 95% of the bootstrap distribution for both 40% and 75% RH.

![Histograms of maximum depths from 1000 bootstrap samples](image)

Figure 6: Histograms of maximum depths in 1000 bootstrap samples. The middle 95% of the distribution is indicated with a horizontal line. The true maximum from the data is marked with an "x." Left: 40% RH. Right: 75% RH.
Table 3 provides a summary of the bootstrap results. Both the quantile and mean method estimate the maximum reasonably well, with the quantile method performing better for the 40% RH data and the mean method performing better for the 75% RH data. The coverage probabilities for the 95% prediction interval are somewhat less than 95%, because of the random measurement error added to the simulated pit depths.

<table>
<thead>
<tr>
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<th>40% RH</th>
<th>75% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean True maximum</td>
<td>57.514</td>
<td>64.032</td>
</tr>
<tr>
<td>Mean estimated maximum (quantile)</td>
<td>57.523</td>
<td>61.522</td>
</tr>
<tr>
<td>Mean estimated maximum (mean)</td>
<td>58.982</td>
<td>64.189</td>
</tr>
<tr>
<td>Percent coverage by 95% prediction interval</td>
<td>91.7</td>
<td>87.8</td>
</tr>
</tbody>
</table>

5 Sensitivity Analysis

The estimated maximum depth is determined by combination of assessments $\hat{\alpha}, \hat{\beta}, \hat{\gamma}, \hat{\delta}$. To investigate the sensitivity of the results to these estimates, we computed 95% confidence intervals for each parameter. The confidence interval for $\alpha$, for example, was $\hat{\alpha} \pm 1.96s_\alpha$, where $\hat{\alpha}$ is the estimate from the real data and $s_\alpha$ is the standard deviation of the 1000 bootstrap estimates of $\alpha$.

<table>
<thead>
<tr>
<th></th>
<th>40% RH</th>
<th>75% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>(20.700, 22.641)</td>
<td>(0,113.806)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>(0.263, 0.311)</td>
<td>(0.330, 0.514)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>(0.221, 0.361)</td>
<td>—</td>
</tr>
<tr>
<td>$\delta$</td>
<td>(0.264, 0.493)</td>
<td>(0.28, 1.66)</td>
</tr>
</tbody>
</table>

For the bootstrap simulation, $\hat{\alpha}$ is the true value, For 75% RH the upper confidence limit represents an unusually high estimate and the lower confidence limit represents an unusually low estimate.

For the 75% data, we assumed $\gamma$ to be 0, so there is no confidence interval for $\gamma$. Because the amount of data is relatively small, the standard deviations for $\hat{\alpha}$, and $\hat{\delta}$ are quite large, and the intervals as originally computed contained negative values, which are unrealistic. We therefore set the lower confidence limits to 0.
Because two of the confidence intervals for the 75% data were very large, we restricted our sensitivity analysis to the 40% data. For each parameter, we considered the upper confidence limit to be the “high” estimate, and the lower confidence limit to be the “low” estimate. We computed the cdf of pit depths under 16 scenarios, with each scenario corresponding to one of the 16 combinations of high and low values for the parameters. We then computed the estimated maximum depth, using the quantile method, for each scenario. Table 5 presents the results. The 95% prediction interval based on the real data was (52, 65) (see Table 2). The estimated maximum pit depth were outside the real data only in two scenarios cases for lower limits of $\alpha$, $\beta$, $\gamma$ and upper limit $\delta$, and lower limit $\alpha$, $\beta$, and upper limit of $\gamma$ and $\delta$. In both cases the maximum pits depth were underpredicted the lower bounds by 4%. In all other scenarios the maximum pits are within the actual interval. The sensitivity results also indicated that $\delta$ parameter is the most sensitive one. Both the quantile and mean method estimate the maximum pits depth are very good with less than 3% for 40%, and less than 4% for 75% RH, quantile.

### Table 5: Quantile estimate of max depth for extreme values of parameters

<table>
<thead>
<tr>
<th>Lower Limit</th>
<th>Upper Limit</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \beta \gamma \delta$</td>
<td>$-$</td>
<td>54</td>
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<td>$\alpha \beta \gamma$</td>
<td>$\delta$</td>
<td>50</td>
</tr>
<tr>
<td>$\alpha \beta \delta$</td>
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<td>54</td>
</tr>
<tr>
<td>$\alpha \beta$</td>
<td>$\gamma \delta$</td>
<td>50</td>
</tr>
<tr>
<td>$\alpha \gamma \delta$</td>
<td>$\beta$</td>
<td>59</td>
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<tr>
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<tr>
<td>$\alpha$</td>
<td>$\beta \gamma \delta$</td>
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</table>

<table>
<thead>
<tr>
<th>Lower Limit</th>
<th>Upper Limit</th>
<th>Maximum</th>
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<tbody>
<tr>
<td>$\beta \gamma \delta$</td>
<td>$\alpha$</td>
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</tr>
<tr>
<td>$-\alpha \beta \gamma \delta$</td>
<td>58</td>
<td></td>
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</tbody>
</table>

### 6 Conclusions

The distribution of pit depths can be well described by a proposed stochastic model that model’s initiation and growth as heterogeneous Poisson processes, with initiation rates proportional to the surface area that is un-pitted and growth rates decreasing loglinearly in time.

The model we describe fits the distribution of pits very well retrospectively. Extrapolating forward, the predictions of maximum depth after six months are still accurate. In particular, a 95% prediction interval
has a high probability of capturing the true maximum, even when measurement error is taken into account.

The major limitation of this work is that it is based on a small number of samples prepared under similar conditions. Further work with larger samples in a wider variety of conditions will provide more clarity regarding the general usefulness of this method for various environmental conditions.

The methodology developed in this paper is flexible and the parameters can be adjusted to initial experimental time steps sets of the data depends on the experiments conditions, for realistic predicting the maximum pits growth rate for longer time, including confidence interval. As it was shown in this paper for 45% RH and 75% RH data cases.

Acknowledgments

The authors thanks to Timothy Weirich, Jenifer Locke and Eric J. Schindelholz for providing experimental data for validating the methodology in this paper. This work supported by U.S. Department of Energy, Nuclear Energy University Programs (NEUP), under award # DE-NE000842.
References


31. Private communications with Fontana Corrosion Center, Department of Materials Science and Engineering, The Ohio State University Ohio State University.
Chapter 9
PROJECT TITLE – Innovative Approach to SCC Inspection and Evaluation of Canister in Dry Storage

Authors (Institution):
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Mr. Leonardi Tjayadi, Graduate Student

Tasks Titles: Accelerated Crack Growth Experiments
Subtask Titles:
1. Evaluation of $K_{\text{ISCC}}$ and crack growth rates in 304H and 304L stainless steel
2. Evaluation of $J_{\text{ISCC}}$ using unloading compliance technique under 3-point bend loading

1. Objective and Overview
The objective of the project is to apply fracture mechanics-based approach to investigate chloride induced stress corrosion cracking (CISCC) in 304 stainless steel (SS) used in spent nuclear fuel (SNF) dry storage canisters. The project consists of determining the crack growth rate and the stress intensity factor under marine environment ($K_{\text{ISCC}}$) for a given load and crack size. Another objective is to evaluate $J_{\text{ISCC}}$ in marine environment following unloading compliance technique using three-point bend specimens.

The crack growth experiments were performed with sensitized SS304H under the following conditions: (a) substitute ocean water at 22, 37 and 60 °C, (b) NaCl and HCl solution at 60 °C and (c) MgCl$_2$ brine at 60 °C. In addition, crack growth experiments were also conducted on sensitized SS304L under substitute ocean water at 21 °C and 38 °C followed by higher concentration of NaCl solution at 39 °C. With regards to the $J_{\text{IC}}$ experiment, efforts were made to determine $J_{\text{IC}}$ using smaller Charpy specimen (55 x 5 x 5 mm) instead of the standard Charpy size specimen to match the capability of the mechanical testing unit available in the Nuclear Materials Laboratory at NCSU. However, it was noted that the material is too ductile to be used for the $J_{\text{IC}}$ experiment and thus the $J_{\text{ISCC}}$ could not be determined by the unloading compliance technique and thus it is proposed to
use the $K_{ISCC}$ values to evaluate $J_{ISCC}$. It is suggested that $J_{ISCC}$ could be determined using the WOL specimens that were already exposed to SCC.

2. Summary of Accomplished Tasks and Open Issues
Crack growth experiments were performed with sensitized SS304H under substitute ocean water at 22, 37 and 60 °C to determine the effect of temperature on crack growth rate. The experiments was conducted on wedge opening loading (WOL) specimens under NaCl and HCl solution to assess the effect of pH on crack growth rate. The effect of chloride on crack growth rate was investigated by comparing the average crack growth rate from the experiments under substitute ocean water and MgCl$_2$ brine. Crack growth experiments were also performed with sensitized SS304L to examine the effect of carbon on corrosion resistance. Effect of salt concentration on crack growth rate was also attempted. All experiments were conducted with an initial stress intensity factor of around 30 MPa m$^{1/2}$. The average crack growth rates were comparable to the ones reported in the literature. The experiment with sensitized SS304H at 37 °C was conducted for more than two months so that $K_{ISCC}$ could be determined. Considering the available amount of time for the project and the time required to perform a crack growth experiments until a $K_{ISCC}$ value is produced, the other experiments were performed to obtain the average crack growth rates. Attempts to determine $J_{IC}$ using unloading compliance technique were not fruitful apparently due to the relatively large ductility of the as-received stainless steel specimens and thus, attention and efforts have been invested more in the crack growth experiments using sensitized SS304H/L materials. However, it is shown that $J_{ISCC}$ could be evaluated from the $K_{ISCC}$ values reported here.

3. Progress and Status

3.1 Introduction
After submersion of at least five years in spent fuel pools (Fig. 1 [1]), the SNF in the US is transferred to Independent Spent Fuel Storage Installations (ISFSI) for storage for more than several decades (with discussions currently underway to extend the life beyond 100 years) in horizontal and/or vertical dry storage canisters typically made of austenitic stainless steels. As seen in Fig. 2, the dry storage canisters are then encapsulated in a dry storage cask (DSC) equipped with air ventilation for cooling [2]. The spent fuel storage facilities in the US as shown in Fig. 3 are usually located next to the ocean (Fig. 4) which then can cause the dry storage canisters to be
exposed to ambient site conditions through the air ventilation [3]. National Atmospheric Deposition Program reported that the majority of ISFSI locations in the US contain high levels of chloride salts [4]. The combination of the DSC equipped with air ventilation for natural cooling and the high level of chloride salts may cause the salts to be deposited on the dry storage canister leading to possible chloride-induced stress corrosion cracking (CISCC) [5]. In fact, in a recent study regarding the degradation mode of materials used in ISFSI, EPRI recommended several potential degradation mechanisms (Fig. 5) and CISCC topped the list [6]. Recent canister inspections have shown that chloride salts were present on the surface of the in-service canisters in near-marine settings [7-9].
Mathematically, the crack growth rate can be expressed as \[8,9,10\]

\[
\frac{dx_{\text{crack}}}{dt} = \dot{x}_{\text{crack}} = \alpha_{\text{crack}} f(T) f(K) f(R_a) f([\text{Cl}^-]) f(m_{\text{Cl}}) f(pH) f(\sigma_y) \tag{1}
\]

where the crack growth rate \(\dot{x}_{\text{crack}}\) is dependent upon the crack growth rate at a fixed reference set of conditions \(\alpha_{\text{crack}}\), temperature \(T\), stress intensity factor \(K\), degree of sensitization \(R_a\), chloride concentration \([\text{Cl}^-]\), chloride mass per unit area \(m_{\text{Cl}}\), pH of the solution and yield stress \(\sigma_y\) of the material. Sandia National Laboratory has considered the effects of stress intensity factor and temperature by using the power-law dependence and Arrhenius relationship, respectively \[10\]

\[
\frac{dx_{\text{crack}}}{dt} = \alpha_{\text{crack}} \cdot \exp \left[ -\frac{Q}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \cdot (K - K_{\text{th}})^{\beta_{\text{crack}}} \tag{2}
\]

where \(Q\) = the activation energy for crack growth
\(R\) = universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\) or 1.987 cal mol\(^{-1}\) K\(^{-1}\))
\(T\) = temperature (K)
\(T_{\text{ref}}\) = 60 °F = 15.6 °C
\(K_{\text{th}}\) = threshold stress intensity factor for SCC
\(\beta_{\text{crack}}\) = stress intensity factor exponent

Evidently, the use of mathematical model of crack-growth expressed by Eq. (2) would require, among many parameters, knowledge of threshold stress intensity factor. In non-corrosive media, \(K_{\text{th}}\) corresponds to plane strain fracture toughness (Fig. 6) denoted by \(K_{IC}\) which is valid when the specimen thickness, \(B > 2.5 \left( \frac{K_{IC}}{\sigma_y} \right)^2\) (Fig. 7) whereas in corrosive media, \(K_{\text{th}}\) becomes \(K_{ISC\text{C}}\), the stress intensity factor in SCC environment \[10\]. Thus, \(K_{ISC\text{C}}\) is one of the important parameters to be measured in the project along with the crack growth rate, \(\dot{x}_{\text{crack}}\).
The linear elastic fracture mechanics (LEFM) is applicable to materials that exhibit brittle fracture behavior. Fracture toughness of materials that exhibit large-scale plasticity during deformation cannot be characterized by LEFM is characterized by elastic-plastic fracture mechanics (EPFM) where the two techniques of importance are J-integral and crack-tip-opening displacement (CTOD). J-integral is defined as the rate of change of strain energy with respect to crack length or the energy available for crack extension in inelastic materials [10]). The determination of \( K_{\text{ISCC}} \) or \( J_{\text{ISCC}} \) by fracture mechanics will be useful in predicting the crack growth rate of a structure under certain loading conditions which in turn will help in assessing its useful life in a marine environment. The following sections include the experimental results that have been achieved up-to-date.

3.2 Experimental Setup and Procedure

3.2.1 Evaluation of \( K_{\text{ISCC}} \) and crack-growth measurement

3.2.1.1 Corrosion Chamber

To investigate SCC behavior of SS304H and SS304L which have been used for fabricating dry storage canisters, a corrosion chamber was built at North Carolina State University. A CAD drawing of the corrosion chamber is included in Figure 8a. The actual chamber is shown in Figure 8b. The length, width, and depth of the chamber were 762 x 305 x 305 mm (30 x 12 x 12 in.), respectively. The size of the chamber is sufficient to conduct SCC experiments of up to four specimens simultaneously. This feature will come in handy when evaluating many specimens.
either in different conditions or for measuring scatter in data points under the same condition. The sides and bottom of the chamber were fabricated from polycarbonate and the internal edges of the chamber were sealed using a marine grade silicone-based sealant. For suspending samples inside the chamber, a hanger was built with its ends resting on the top portion of the sides of the chamber opposite to each other. The hanger is equipped with four clamps with provisions for suspending samples in the marine solutions and also managing input/output signal wires from/to the samples. Both the hanger and clamps are made of garolite (also known as Phenolic), a polymer matrix composite made of glass fibers impregnated with epoxy resins. It is a strong, stiff, electrically non-conducting, and highly corrosion resistant material.

![Figure 8](image_url) (a) A CAD model showing design of the corrosion chamber and (b) a photograph showing the corrosion chamber built following the CAD design shown in (a).
3.2.1.2 Wedge Opening Loading Specimen

In the study of SCC using fracture mechanics-based approach, a wide variety of specimens are used. Compact tension, single edge bend, and disk-shaped compact specimens are some specimen geometries most commonly used in the evaluation of fracture toughness. ASTM standard E399–12 can be referred to for further details on these specimens [12]. Wedge opening loading (WOL) specimen was developed in response to very large sample size requirement for conventional specimens for evaluating $K_{IC}$ of medium to low strength metallic materials [13].

The WOL specimen geometry and related dimensions are shown in Figure 9. A combination of CNC and electro-discharge machining (EDM) techniques were used for specimen preparation. While the notch of the WOL specimen was prepared using EDM, the rest was made using CNC machining. The WOL specimen will be loaded using an instrumented bolt which goes inside the specimen through the tapped hole labeled as 1 and impinges on the flat portion on a pin inserted through the hole labeled 2 in Figure 9. The drawing of the pin is shown in Figure 10. The WOL and pin are made of SS304 H – the material sent by CSM.

![Figure 9 2-D and 3-D drawing showing WOL specimen geometry and dimensions](image-url)
A photograph of the WOL specimen is shown in Figure 11a along with the pin for which the drawing is shown in Figure 10. A close-up views of notched region of the WOL specimen at two different magnifications are shown in Figures 11b and 11c. In this case, the notch root radius was measured and was found to be equal to ~193 µm (Figure 11c).

Figure 11 (a) Different views of WOL samples prepared from SS 304 H alloy supplied by Colorado School of Mines, Golden, (b) optical macrograph showing tip region of the WOL specimen, and (c) A magnified view of the notch tip showing the shape of the tip for measuring the radius of the tip (radius = ~193 µm).

3.2.1.3 Instrumented Bolt for Loading WOL Specimen

For loading WOL specimen to a desired level, an instrumented bolt will be used. A drawing of the instrumented bolt (procured from Strainsert company) with pertinent details is given in Figure 12. The labels shown in the drawing provide the details of the design and dimensions of the
instrumented bolt. It is made of 17-4 PH stainless steel and designed to take a compressive loads to 2400 lb. The calibration of the bolt was carried out by the manufacturer and the calibration values are included in Table I and exhibited linear behavior (Fig. 13).

![Instrumented bolt designed by Strainsert company](image)

**Table 1 Strainsert Calibration Chart**

<table>
<thead>
<tr>
<th>Test Load (lbf)</th>
<th>Test Load (N)</th>
<th>Straight Line Signal (mV/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>480</td>
<td>2135.15</td>
<td>0.515</td>
</tr>
<tr>
<td>960</td>
<td>4270.29</td>
<td>1.029</td>
</tr>
<tr>
<td>1440</td>
<td>6405.44</td>
<td>1.544</td>
</tr>
<tr>
<td>1920</td>
<td>8540.59</td>
<td>2.058</td>
</tr>
<tr>
<td>2400</td>
<td>10675.73</td>
<td>2.573</td>
</tr>
</tbody>
</table>

![Linear Fit of Sheet1 B"Signal"

**Figure 13 Instrumented bolt straight line signal as a function of test load.**
3.2.1.4 Fatigue Pre-cracking

A 2D CAD drawing model of the wedge opening loading (WOL) SS304 specimens used in the project along with dimensions in inches is shown in Fig. 14a. Note that the dimensions of the actual WOL specimen differed from the original dimensions shown in Fig. 9 to accommodate instrumented bolt load limit to develop sufficient level of stress intensity. An actual machined WOL specimen is shown in Fig. 14b with the radius of the notch ranging from 150-250 μm where the variation of the notch radius comes from the uncertainty in the fabrication of the WOL specimens. The WOL specimens were fatigue pre-cracked using a fatigue machine from Test Resources model 910LX15 as shown in Fig. 15 to produce the desirable sharpness. A fatigue pre-cracked specimen is shown in Fig. 16.

Figure 14 (a) Dimension of WOL specimen in inches and (b) WOL specimen

Figure 15 Fatigue pre-crack experimental setup

Figure 16 A fatigue pre-cracked WOL specimen
The fatigue pre-crack experiments followed ASTM E399-12 [12], E1820-15 [14] and E1681-03 [15] where the WOL specimen was treated as a compact tension (CT) specimen and the stress intensity factor was calculated from the ASTM E399-12,

\[
K_Q = \frac{P_Q}{\sqrt{B B_N V W}} f\left(\frac{a}{W}\right)
\]

\[
f\left(\frac{a}{W}\right) = \frac{\left(2 + \frac{a}{W}\right) 0.886 + 4.64 \frac{a}{W} - 13.32 \left(\frac{a}{W}\right)^2 + 14.72 \left(\frac{a}{W}\right)^3 - 5.6 \left(\frac{a}{W}\right)^4}{\left(1 - \frac{a}{W}\right)^{3/2}}
\]

where \(P_Q\) = load applied (N or lbf)

\(B\) = specimen thickness (m or in)

\(B_N\) = specimen thickness between the roots of the side grooves (m or in)

\(W\) = specimen width (m or in)

\(a\) = crack length (m or in)

The fatigue pre-cracking experiment was performed under a sinusoidal cyclic loading at a load ratio of 0.1 with maximum applied load of 6000 N giving a mean applied load of 3300 N and a load amplitude of 2700 N. Once the fatigue pre-crack of desired length was produced at the tip of the notch, the fatigue pre-crack lengths of the WOL specimens were measured using an optical microscope (Fig. 17).
3.2.1.5 Kiscc Measurement Using Direct-Current Potential Drop Technique

Fracture mechanics-based SCC study involves monitoring of load, load line displacement (or crack mouth opening displacement), and crack length with time. There are many ways crack length can be monitored – optical microscopy, scanning electron microscopy (SEM), replication, potential difference, and ultrasonics. Due to its simplicity, the direct-current potential drop (DCPD) technique has been widely used for detecting crack initiation and monitoring crack growth. This technique involves supplying a constant current through the specimen and measuring potential drop as crack propagates. The principle of DCPD as per ASTM E647 – 15 is as follows [16].

“Determining crack size from electric potential measurements relies on the principle that the electrical field in a cracked specimen with a current flowing through it is a function of the specimen geometry, and in particular the crack size. For a constant current flow, the electric potential or voltage drop across the crack plane will increase with increasing crack size due to modification of the electrical field and associated perturbation of the current streamlines. The change in voltage can be related to crack size through analytical or experimental calibration relationships.”

For prediction of crack length, a calibration curve has been developed for the specimen under consideration. Johnson [17] suggested that such calibration curves are independent of chemical composition, heat-treatment, and thickness.

For the development of calibration chart, in the present case, the DCPD measurement unit involved a DC power supply from Kikusui (model number of PAT160-50T) and a nanovoltmeter from Keithley (model number of 2182A). The wires from the Keithley nanovoltmeter are attached to the WOL specimen as shown in Fig. 18 and Fig. 19 for measurements in air and marine environments respectively. During the DCPD measurement, a 0.2V and 5A current were supplied by the Kikusui DC power supply and a reading was obtained in V from the Keithley nanovoltmeter up to six decimal points. Once the fatigue pre-crack length has been measured, the fatigue pre-cracked WOL specimen was setup as shown in Fig. 18 for DCPD measurement. After a reading has been recorded, the fatigue pre-cracking experiment was repeated (Fig. 15) for the second time along with fatigue pre-crack length (Figs. 17) and DCPD measurement (Figs. 18 & 19) to generate a calibration curve consisting of several data points.

For crack growth measurement, the DCPD measurement unit shown in Fig. 20a involves two DC power supplies from Kikusui (model number of PAT160-50T) for measurement of crack growth,
BK Precision to provide electrical current for measuring applied load and two nanovoltmeters from Keithley (with a model number of 2182A) to measure the potential drop of the crack growth and from Fluke model 287 to measure the potential drop of the applied load throughout the experiment. The Keithley nanovoltmeter is attached to the WOL specimen and the load is applied through an instrumented bolt as shown in Fig. 20b. During the DCPD measurement, electrical current is supplied by the Kikusui DC power supply and readings of crack growth and applied load are obtained in mV from the Keithley nanovoltmeter up to six decimal points and from Fluke nanovoltmeter up to three decimal points, respectively.

![Figure 18 DCPD measurement in air for calibration chart](image1)

![Figure 19 DCPD experiment setup in marine environment for calibration chart](image2)

![Figure 20 (a) Crack growth experimental setup and (b) WOL specimen submerged in marine environment](image3)

The $K_{\text{ISCC}}$ experiment involves loading the specimen such that the stress intensity factor is above $K_{\text{ISCC}}$ and less than $K_{\text{IC}}$. A preliminary calculation has been performed that relates the stress intensity factor with the corresponding applied load for lower and upper limits of crack length of 7.72 and 9.43 mm ($0.45 \leq a/W \leq 0.55$), respectively. By utilizing Eqs. 3 and 4, for a specimen width
of 0.675 in (17.145 mm) and a thickness of 0.625 in (15.875 mm), an applied load can be obtained for a specified value of stress intensity factor for the lower and upper limits of crack length. The crack growth measurement is performed in marine environment (substitute ocean water) using DCPD technique where the fatigue pre-cracked WOL specimen is submerged in the corrosion chamber such that the fatigue pre-crack length is submerged in the marine solution with the notch staying above the surface of the marine solution.

3.2.2 JISCC Method

It was also proposed to use sub-size Charpy specimens to first fatigue pre-crack and then expose them to marine environment for certain time and then evaluate fracture toughness (JISCC) using unloading compliance technique under 3-point bend loading as per the procedures developed at NCSU. A relatively simple experimental system and related computer programs to successfully evaluate the J-integral property of a material by the unloading compliance method at different temperatures and loading rates have been developed at NCSU. A servo-hydraulic testing machine will be used to carry out the J-integral evaluation by three-point bend method according to the ASTM standards. A tension compression loading cage and a three-point bend fixture have already been designed and machined to conform to the ASTM standard specifications. Figure 21 shows a schematic, a photograph of the test apparatus while a CAD design of the only essential part of the fixture is shown in Figure 21b. Load and load-line displacements will be monitored using load cell and an LVDT (shown in Figure 21a) in the load-line. Advantage of this system is that it can be used for high temperature testing as well.

Figure 21 (a) A 2-D drawing of three-point bend fixture, (b) a three-point bend fixture and (c) a CAD drawing of the center of the fixture to place and hold the sample
The determination of $J_{IC}$ and $J_{ISCC}$ can be deduced from the J-R resistance curve that can be constructed from the prediction of the crack length of the specimen at each partial unloading step using the elastic compliance calibration equation expressed as

$$C(a/w) = 0.24 \left( \frac{s}{w} \right) \{1.04 + 3.28 \left( \frac{w}{s} \right) \left( 1 + v^2 \right) \} + 2 \left( 1 - v^2 \right) \left( \frac{s}{w} \right) \left( \frac{a}{w} \right) \{4.21 \left( \frac{a}{w} \right) - 8.89 \left( \frac{a}{w} \right)^2 + 36.9 \left( \frac{a}{w} \right)^3 - 83.6 \left( \frac{a}{w} \right)^4 + 174.3 \left( \frac{a}{w} \right)^5 - 284.8 \left( \frac{a}{w} \right)^6 + 387.6 \left( \frac{a}{w} \right)^7 - 322.8 \left( \frac{a}{w} \right)^8 + 149.8 \left( \frac{a}{w} \right)^9 \} \tag{5}$$

where $s$ is span of the Charpy Impact bar support points, $C(a/W)$ is the normalized plane strain compliance function and other symbols have the same meaning as defined for WOL specimen. To calculate the crack length from the unload-reload cycles, therefore, the respective measured compliances are substituted into the polynomial given in Eq. (5) and an inverse of the equation is obtained for each partial unloading step. A schematic of the load versus load-line displacement curve is shown in Figure 22.

*Figure 22* A schematic of load vs load-line displacement curve

*The J-integral can then be obtained from Figure 22 at any unloading point using the equation,*

$$J = 2 \frac{A_i}{B_{eff} b} \tag{6}$$

where $A_i = \text{the area under the load vs. load-line displacement curve up to the } i^{\text{th}} \text{ step and } b = \text{the initial remaining ligament.}$
Calibration of extraneous compliance and the required corrections are to be taken into account as per the detailed descriptions provided in the references 18-20. Once J-R curves are developed from which $J_{IC}$ can be evaluated, effect of environment will yield the appropriate $J_{ISCC}$ that can be compared to the $K_{ISCC}$ values obtained from WOL specimens. An advantage of using Charpy and subsize Charpy specimens is in plausible extensions to evaluate the effect of neutron irradiation on $J_{ISCC}$ for these stainless-steel welds.

3.3 Results

3.3.1 Evaluation of $K_{ISCC}$ and Crack-Growth Measurements

3.3.1.1 Microstructural characterization of as-received Sample

Prior to the crack growth experiments, the SS304H/L materials received from Colorado School of Mines (CSM) were mechanically polished down to mirror finish and etched with a solution of hydrochloric acid, nitric acid and water of equivalent ratio, cleaned with methanol and deionized water for metallography. The energy dispersive spectroscopy (EDS) in SEM was used to detect the distribution of different elements among different phases present in the alloy as shown in Fig. 23 and 24 for SS304H and L, respectively.

Figure 23 (a) Optical micrograph, (b) elements identified from EDS and (c) intensities of the identified elements through EDS of SS304H
3.3.1.2 Mechanical Properties

Tensile tests were performed at a strain rate of $10^{-3}$s$^{-1}$ in air at room temperature for both SS304H and SS304L each in the rolling (RD) and transverse (TD) directions and the results are tabulated in Table 2.
Table 2 Tensile test results of SS304H/L with the errors indicated inside the brackets

<table>
<thead>
<tr>
<th></th>
<th>Yield Stress (MPa)</th>
<th>UTS (MPa)</th>
<th>Uniform Elongation (%)</th>
<th>Total Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS304H 215 hrs RD</td>
<td>302 (11)</td>
<td>701 (14)</td>
<td>80.8 (5.3)</td>
<td>92.4 (4.6)</td>
</tr>
<tr>
<td>SS304H 215 hrs TD</td>
<td>272 (9)</td>
<td>702 (14)</td>
<td>76.6 (2.8)</td>
<td>84.2 (1.3)</td>
</tr>
<tr>
<td>SS304L 215 hrs RD</td>
<td>264 (15)</td>
<td>670 (7)</td>
<td>84.3 (2.0)</td>
<td>97.7 (0.4)</td>
</tr>
<tr>
<td>SS304L 215 hrs TD</td>
<td>274 (5)</td>
<td>672 (22)</td>
<td>85.7 (4.8)</td>
<td>96.6 (8.4)</td>
</tr>
</tbody>
</table>

3.3.1.3 Calibration Chart

After the steps of the experiment were repeated several times as described in section 3.2.1.5, a calibration curve with a reliable set of data is generated as shown in Fig. 26. The objective of the DCPD measurement is to create a calibration curve for a WOL specimen that will be used to study the SCC behavior of SS304 in marine environments which also requires monitoring of crack-growth during the experiment.

![Calibration curve of potential drop of WOL specimen](image)

Figure 26 Calibration curve of potential drop of WOL specimen as a function of fatigue pre-crack length in air (blue circle) and marine environments (red square and blue triangle).
The values from the DCPD measurements in the marine environment were plotted in the same graph as those in air and are shown in Fig. 26. Clearly, the DCPD measurements in marine environment yield similar results to those in air producing a linear relationship between the potential drop and the fatigue pre-crack length. In the fatigue pre-cracked WOL specimen, as crack increases, resistance increases and therefore, the potential drop increases. This calibration curve was used for the SCC experiments in the project.

3.3.1.4 Crack Growth Experiments
Before using the sensitized SS304H/ L, two crack growth experiments were performed using the non-sensitized SS304 materials. First experiment was conducted with a non-sensitized SS304 material with a fatigue pre-crack length of 2475 μm but the specimen plastically deformed beyond an applied load of 1000 lbf as shown in Fig. 27. Another attempt was made with the same material with a fatigue pre-crack length of 3200 μm and the specimen, again, plastically deformed at 1000 lbf as shown in Fig. 28. Although these two attempts did not produce important outcomes, a particular note is made on the maximum applied load of 1000 lbf for non-sensitized SS304 material for future experiments.

Figure 27 (a) A load applied to a non-sensitized SS304 specimen and (b) a non-sensitized SS304 specimen with a fatigue pre-crack length of 2475 μm failed after 1000 lbf
With the consideration that the non-sensitized SS304 material cannot be loaded beyond 1000 lbf without excessive plastic deformation ahead of the crack tip implying low value for stress intensity factor, the crack growth experiments were then performed with sensitized SS304 H/L. A sensitized SS304H specimen was fatigue pre-cracked to 897 μm and submerged in substitute ocean water (composition given in Table 3) with an applied load of 1872 lbf (34 MPa m¹/²) at room temperature for six weeks. In addition, a calculation was performed to determine the stress intensity factor that corresponds to the initial applied load with an example shown in Table 4.

### Table 3 Chemical composition of the substitute ocean water [21]

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaCl</th>
<th>MgCl₂</th>
<th>Na₂SO₄</th>
<th>CaCl₂</th>
<th>KCl</th>
<th>NaHCO₃</th>
<th>KBr</th>
<th>H₃BO₃</th>
<th>SrCl₂</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (g/L)</td>
<td>24.53</td>
<td>5.20</td>
<td>4.09</td>
<td>1.16</td>
<td>0.695</td>
<td>0.201</td>
<td>0.101</td>
<td>0.027</td>
<td>0.025</td>
<td>0.003</td>
</tr>
</tbody>
</table>

#### 3.3.1.5 Crack growth results (SS304H)

The plots of bolt load and crack length with time in Figs. 29 a and 29 b indicate that the applied load decreases slowly and the crack length remains constant. Thus, the crack did not propagate for the first 300 hrs of the experiment. But the steep decrease in bolt load with time and increase in crack length with time (Figs. 29 c and 29 d) afterwards suggest that crack propagation occurred. The stress intensity factor decreases exponentially with crack extension (Fig. 29e) and further data analyses yielded the average crack growth rate of SS304H at 22 °C under substitute ocean water.
to be $0.975 \times 10^{-10} \pm 9.528 \times 10^{-12}$ m/s which is in good agreement with the average crack growth rate for SS304 at 22 °C as reported by Speidel of $1.438 \times 10^{-10}$ m/s [22].

Table 4 Load calculation as a function of $K_I$ values for a sample with two different crack lengths

<table>
<thead>
<tr>
<th>$K_I$ (MPa√m)</th>
<th>$a_0 = 7.72$ mm</th>
<th></th>
<th>$a_0 = 9.43$ mm</th>
<th></th>
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Figure 29 (a) Bolt load variation with time, (b) crack length variation with time, (c) stress intensity factor exponential fit with time, (d) crack growth linear fit with time, (e) stress intensity factor behavior with crack growth and (f) crack growth rate with stress intensity factor for SS304H under substitute ocean water at 22 °C.

Another experiment was conducted with a sensitized SS304H specimen fatigue pre-cracked to 860 μm and with an applied load of 1730 lbf (31 MPa m$^{1/2}$) submerged in substitute ocean water at 37 °C for nine weeks. As the experiment was conducted at higher temperature, the crack propagation occurred earlier than the previous one at 22 °C. From the bolt load behavior with time in Fig. 30a and crack length versus time in Fig. 30b, crack is noted to propagate after three days of the
experiment. Performing the experiment for a longer time produced a saturation in the behavior of stress intensity factor with time as shown in Fig. 30d giving a threshold stress intensity factor ($K_{\text{ISC}}$) of SS304H at 37 °C under substitute ocean water of 15 MPa m$^{1/2}$. Although there is no direct comparison for $K_{\text{ISC}}$ at this temperature, a fair comparison can be made with that obtained by Speidel for sensitized SS304 in 22% NaCl environment at 105 °C of 9 MPa m$^{1/2}$ [23]. Figure 30f shows that the stress intensity factor decreases in the same manner as in the previous experiment and data analyses from Fig. 30g for SS304H experiment at 37 °C under substitute ocean water produces an average crack growth rate of 3.258x10$^{-10} \pm 9.551x10^{-11}$ m/s.

Another sensitized SS304H specimen was fatigue pre-cracked to 735 μm and submerged in substitute ocean water (composition given in Table 2) with a starting applied load of 24 MPa m$^{1/2}$ at 60 °C. The plots of bolt load and crack length with time in Figs. 31 a and 31 b indicate that the applied load decreases slowly and the crack length remains constant for the first six hours of the experiment. Based on the applied load behavior with time, the stress intensity factor with time was obtained as displayed in Fig. 31c, and Fig. 31d shows the crack growth behavior with time indicating crack growth after six hours (2.2x10$^4$ s). In addition, following crack propagation, the stress intensity factor decreases exponentially with crack extension (Fig. 31e), and crack growth rate behavior with stress intensity factor in Fig. 31f produces an average crack growth rate of SS304H at 60 °C under substitute ocean water of 1.580x10$^{-9} \pm 2.593x10^{-10}$ m/s.
Figure 30 (a) Bolt load behavior with time, (b) crack length behavior with time, (c) stress intensity factor exponential fit with time, (d) threshold stress intensity factor, (e) crack growth exponential fit with time, (f) stress intensity factor behavior with crack growth and (g) crack growth rate with stress intensity factor for SS304H under substitute ocean water at 37 °C.
Figure 31 (a) Bolt load behavior with time, (b) crack length behavior with time, (c) stress intensity factor with time, (d) crack growth with time, (e) stress intensity factor behavior with crack growth and (f) crack growth rate with stress intensity factor for SS304H under substitute ocean water at 60 °C
3.3.1.6 Effect of temperature on crack growth (SS304H)

The temperature dependence of the crack growth rates is described through an Arrhenius equation as expressed by

\[ \frac{da}{dt} = C \exp\left(\frac{-Q}{RT}\right) \]  

(Eq. 7)

where \( \frac{da}{dt} \) = crack growth rate (m/s), \( C \) = an arbitrary constant, \( Q \) = activation energy (J/mol), \( R \) = universal gas constant (8.314 J/mol K) and \( T \) = temperature (K). The activation energy is then evaluated from the slope of the line in Fig. 32 to be 60.9 kJ/mol.

\[
\begin{align*}
\text{Slope} & : -3.11156 \pm 0.00961 \\
\text{Intercept} & : 0.53171 \pm 0.03162
\end{align*}
\]

\[ Q = 60.9 \text{ kJ/mol} \]

This activation energy of 60.9 kJ/mol is in agreement with that obtained by Khatak et al in the range of 50-65 kJ/mol for sensitized SS304 in NaCl environment [24]. Louthan and Devrick associated this activation energy with hydrogen diffusion in iron and austenitic steels [25] implying hydrogen propagation is responsible for the corrosion reaction. Hydrogen is produced in the cathode as shown in Eq. 8 where it then enters the region of higher triaxial tensile stresses in the steel matrix at the crack tip creating corrosion tunnels. These corrosion tunnels in turn initiate crack which then sharpen the crack tip thereby increasing the stress concentration. Hydrogen then segregates at slip bands and grain boundaries ahead of the crack tip separating the grain boundaries to produce intergranular fracture [26]. This propagating crack caused by crack-tip deformation produces brittle fracture as encountered in in-service structures [27].
Anodic reaction: \( \text{Fe (s)} \rightarrow \text{Fe}^{2+} \text{(aq)} + 2e^- \)

Cathodic reaction: \( 2 \text{H}_2\text{O (l)} + 2 \text{e}^- \rightarrow \text{H}_2 \text{(g)} + 20\text{H}^- \text{(aq)} \)

Overall reaction: \( \text{Fe(s)} + 2\text{H}_2\text{O (l)} \rightarrow \text{Fe}^{2+} \text{(aq)} + \text{H}_2 \text{(g)} + 20\text{H}^- \text{(aq)} \)  \hspace{1cm} (Eq. 8)

3.3.1.7 Effect of temperature on crack initiation (SS304H)

Figure 33 shows time for crack initiation versus temperature. As hydrogen is produced from the corrosion reaction, temperature dictates the speed of the reaction kinetics of hydrogen, i.e. temperature determines the speed of the hydrogen transport to the crack tip for crack initiation and once the crack initiates, hydrogen diffuses through the grain boundaries for crack propagation. The higher the temperature, the faster the hydrogen transport to the crack tip as indicated by the crack initiation time and faster the hydrogen propagation through grain boundaries as shown by the crack growth rates. Andresen confirms the influence of temperature on crack initiation and crack growth in his study with sensitized SS304 [28].

![Figure 33 Relationship of crack initiation time with temperatures for SS304H under substitute ocean water](image)

3.3.1.8 Effect of carbon concentration on crack growth (SS304L)

To determine the effect of carbon content on corrosion resistance, two experiments were conducted with sensitized SS304L specimens, one fatigue pre-cracked to 1450 μm with an initial applied load of 1712 lbf (34.3 MPa m\(^{1/2}\)) and the other one fatigue pre-cracked to 980 μm with an initial applied load of 1545 lbf (28.6 MPa m\(^{1/2}\)) both submerged in substitute ocean water at temperatures of 21
℃ and 38 °C, respectively. Data analyses yielded an average crack growth rate of $3.064 \times 10^{-11} \pm 4.009 \times 10^{-12}$ m/s for SS304L experiment at 21 °C and $2.181 \times 10^{-10} \pm 1.975 \times 10^{-11}$ m/s at 38 °C. These average crack growth rates are lower compared to those for SS304H indicating that the lower the carbon content, the better the corrosion resistance and therefore, the smaller the crack growth rate. The results from the experiments with sensitized SS304L are presented in Fig. 34 and 35, respectively.

Figure 34 (a) Bolt load behavior with time, (b) crack length behavior with time, (c) stress intensity factor with time, (d) crack growth with time, (e) stress intensity factor behavior with
crack growth and (f) crack growth rate with stress intensity factor for SS304L under substitute ocean water at 21 °C

Figure 35 (a) Bolt load behavior with time, (b) crack length behavior with time, (c) stress intensity factor with time, (d) crack growth with time and (e) crack growth rate with stress intensity factor for SS304L in 42 g/L substitute ocean water at 38°C

3.3.1.9 Effect of salt concentration on crack growth (SS304L/H)

An experiment was carried out to investigate the effect of salt concentration on crack growth rate with sensitized SS304L at 39 °C in a higher salt concentration of 126 g/L NaCl. The specimen was
fatigue pre-cracked to 732 μm with an initial applied load of 1631 lbf (28.9 MPa m$^{1/2}$) and yielded an average crack growth rate of $1.985 \times 10^{-10} \pm 2.603 \times 10^{-11}$ m/s (Fig. 36e) indicating that higher salt concentration does not increase the crack growth rate. However, the crack initiation occurred faster at higher salt concentration (17.6 hrs) compared to the experiment with sensitized SS304L at 38 °C in 42 g/L substitute ocean water (27.5 hrs). Therefore, the higher the salt concentration is, the faster the crack initiation.
To inspect whether the chlorine in MgCl₂ brine is more aggressive than that in NaCl which was presumed to contribute to the higher crack growth rate in MgCl₂ brine [23], an experiment was implemented with sensitized SS304H at 60 °C in MgCl₂ brine. The specimen was fatigue pre-cracked to 700 μm and an initial load of 22 MPa m¹/² was applied. An average crack growth rate of $1.017 \times 10^{-9} \pm 1.052 \times 10^{-10}$ m/s was obtained from Fig. 37e which is not higher than that of sensitized SS304H under substitute ocean water at the same temperature of 60 °C. This suggests that the chlorine in MgCl₂ brine does not contribute to the higher crack growth rate as proposed by Speidel [23]. As a matter of fact, Speidel conducted his experiments at 105 °C with NaCl and 130 °C with MgCl₂ brine which resulted in the higher crack growth rate under MgCl₂ brine due to its higher operating temperature.

### 3.3.1.10 Effect of pH on crack growth (SS304H)

An experiment was carried out with sensitized SS304H under NaCl + 3mL/L HCl solution at 60 °C to study the effect of pH on crack growth rate with the experimental results shown in Figs. 38. The specimen had a fatigue pre-crack length of 847 μm and the experiment began with an initial applied load of 24.4 MPa m¹/². Crack growth data are shown in Fig. 38 and an average crack growth rate of $2.146 \times 10^{-9} \pm 1.190 \times 10^{-10}$ m/s was achieved (Fig. 38e) from the experiment which is significantly higher than that with sensitized SS304H under substitute ocean water at 60 °C. One plausible reason for the higher average crack growth rate is the lower pH (0.9) of the solution indicating that more hydrogen exists in the solution which act as a catalyst for the crack propagation apart from the operating temperature.
Figure 37 (a) Bolt load behavior with time, (b) crack length behavior with time, (c) stress intensity factor with time, (d) crack growth with time and (e) crack growth rate with stress intensity factor for SS304H at 60 °C in MgCl₂ brine.
Figure 38 (a) Bolt load behavior with time, (b) crack length behavior with time, (c) stress intensity factor with time, (d) crack growth with time and (e) crack growth rate with stress intensity factor for sensitized SS304H under NaCl + 3mL/L HCl solution at 60 °C

3.3.1.11 Microstructural Characterization following Crack Growth Experiments
After the crack growth experiments, the specimens were cleaned with acetone and observed under microscope for crack growth measurement. Subsequently, the specimen was etched with the same solution as mentioned previously to observe the nature of crack propagation. Although the specimens were plastically deformed during loading for the two crack growth experiments with non-sensitized SS304 material and crack growth rate could not be obtained, they were still
submerged under substitute ocean water to investigate the material behavior under marine environment. After 12 days of submersion, the non-sensitized specimen exhibited pitting corrosion as observed in Fig. 39.

![A non-sensitized SS304 specimen with pitting corrosion after submersion in marine environment](image.png)

Figure 39 A non-sensitized SS304 specimen with pitting corrosion after submersion in marine environment

Optical microscopy was also performed on the sensitized SS304H specimen submerged in substitute ocean water at 22 °C. Figure 40 illustrates that the stress corrosion cracking in marine environment does not only open the crack but also produce branching at the crack tip. Crack length measurement from the micrograph yielded a value of 1310 μm indicating a crack growth of 413 μm (after subtracting the fatigue pre-crack length of 897 μm) while the DCPD measurement yielded a crack growth of 405 μm yielding a good agreement. Observation of crack propagation under a metallurgical microscope indicates that majority of the crack propagation occurred intergranularly as displayed in Fig. 41.
The crack growth experiment of sensitized SS304H at 37 °C corroded the entire WOL specimen as illustrated in Fig. 42a. Crack length measurement from the micrograph yielded a value of 2,775 μm indicating a crack growth of 1,915 μm whereas the DCPD measurement yielded a crack growth of 1,840 μm again in good agreement. Observation under metallurgical microscope shows most of the cracks propagated intergranularly (Fig. 43 a-d).
Figure 42 (a) A WOL specimen of SS304H after nine weeks under substitute ocean water at 37 °C and (b) crack length measurement of 2775 μm under a metallurgical microscope.

Figure 43 (a)-(d) Intergranular crack propagation of SS304H after submersion in marine environment for nine weeks at 37 °C.

Figure 44a shows the condition of the WOL specimen after the experiment on the sensitized SS304H specimen submerged in substitute ocean water at 60 °C while Fig. 45a and b illustrate that the stress corrosion cracking in marine environment opened the crack with branching of the crack as in the previous experiments. Crack length measurement from the micrograph yielded a value of 1377 μm as displayed in Fig. 44b indicating a crack growth of 642 μm (after subtracting the fatigue pre-crack length of 735 μm) while the DCPD measurement yielded a crack growth of...
615 μm. Intergranular crack propagations are shown in Figs. 45c and 45d for SS304H specimen tested at 60 °C.

Figure 44 (a) Conditions of SS304H WOL specimen after the experiment under substitute ocean water at 60 °C and (b) a total crack length of 1377 μm was measured after the experiment

Figure 45 (a) and (b) Cracked open SS304H and branching of the crack, (c) and (d) intergranular crack propagation after experiment at 60 °C
Meanwhile, the crack growth experiment of sensitized SS304L at a temperature of 21 °C produces a total crack length of 1535 μm from the micrograph as shown in Fig. 46 indicating a crack growth of 85 μm whereas the DCPD measurement yielded a crack growth of 75 μm.

Figure 46 A measurement of total crack length of 1535 μm for a WOL specimen of SS304L under substitute ocean water at 21 °C under a metallurgical microscope

Figure 47a exhibits the condition of WOL specimen after the crack growth experiment of sensitized SS304L at a temperature of 38 °C and Fig. 47b illustrates a crack growth of 277 μm from the micrograph which agrees well with the crack growth from the DCPD measurement of 298 μm.

Figure 47 (a) Condition of WOL specimen after the experiment and (b) crack growth measurement of 277 μm using optical microscopy of sensitized SS304L at 38 °C in 42 g/L substitute ocean water
On the other hand, the condition of WOL specimen after the crack growth experiment of sensitized SS304L at a temperature of 39 °C in 126 g/L NaCl solution is included in Fig. 48a while Fig. 48b displays a crack growth of 444 μm from the micrograph matching the crack growth from the DCPD measurement of 443 μm.

![Image of WOL specimen condition and crack growth](image)

Figure 48 (a) Condition of WOL specimen after the experiment and (b) crack growth of 444 μm using optical microscopy of sensitized SS304L at 39 °C in 126 g/L NaCl solution

The crack growth experiment of sensitized SS304H in MgCl₂ brine at a temperature of 60 °C grew the crack by 390 μm from the micrograph as shown in Fig. 49 which conforms to the DCPD measurement of 390.3 μm.

![Image of MgCl₂ brine experiment](image)

Figure 49 A crack growth of 390 μm after the experiment in MgCl₂ brine at 60 °C

### 3.3.1.12 J_{ISC} Experiment

Several attempts were made on the J_{IC} experiments with a tensile testing machine (Instron 5566) as well as with a creep-fatigue machine from TestResources® with the latter being the preferred
instrument since there is no time lapse between data recordings. To-date, no satisfactory results have been obtained on Charpy and sub-size Charpy size specimens in 3-point bend mode wherein the samples fractured at the maximum load with no observable decreases in the compliance indicating no crack growth during these tests as illustrated in Fig. 50 and Fig. 51 for constant loading and constant displacement methods respectively. It is presumed that the material used for the JIC experiment is too ductile and/or a new design of the test jig is needed; lack of sufficient funds precluded further work along these lines. The erroneous results obtained to-date are not being reported here.

Although JIC experiment using unloading compliance technique did not work, a calculation of J_{ISCC} is shown using the obtained data from the crack growth experiment performed long enough to produce K_{ISCC} value, that is the crack growth experiment using sensitized SS304H under substitute ocean water at 37 °C. Using

\[ J = \frac{K^2 (1-v^2)}{E} \]  

(Eq. 9)

and \( K_{ISCC} = 15 \) MPa m\(^{1/2}\), \( v = 0.3 \) and \( E = 200 \) GPa gives \( J_{ISCC} = 1023.75 \) J/m\(^2\).

Figure 50 (a) Loading and unloading of charpy specimen and (b) compliance as a function of LVDT displacement for the constant loading method

Figure 51 (a) Loading and unloading of charpy specimen and (b) compliance as a function of LVDT displacement for constant displacement method
### Table 5 Summary of crack growth experiments

<table>
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<th>Specimen</th>
<th>Temp (°C)</th>
<th>Environment</th>
<th>pH</th>
<th>Salt Conc. (g/L)</th>
<th>Average da/dt (m/s)</th>
<th>Average da/dt (mm/year)</th>
<th>Crack Initiation (hrs)</th>
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<td>304H</td>
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<td>0.975 x 10⁻¹⁰ ± 9.528 x 10⁻¹²</td>
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<tr>
<td>304H</td>
<td>37.2 ± 0.9</td>
<td>Substitute ocean water</td>
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<td></td>
<td>3.258 x 10⁻¹⁰ ± 9.551 x 10⁻¹¹</td>
<td>10.27 ± 3.01</td>
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<tr>
<td>304H</td>
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<td>8.2</td>
<td>42</td>
<td>1.580 x 10⁻⁹ ± 2.593 x 10⁻¹⁰</td>
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<td>6.1</td>
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<tr>
<td>304L</td>
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<td>3.064 x 10⁻¹¹ ± 4.009 x 10⁻¹²</td>
<td>0.97 ± 0.13</td>
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<tr>
<td>304L</td>
<td>38.4 ± 0.7</td>
<td></td>
<td></td>
<td></td>
<td>2.181 x 10⁻¹⁰ ± 1.975 x 10⁻¹¹</td>
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<td></td>
<td>6.1 mol/kg</td>
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<td>2.146 x 10⁻⁹ ± 1.190 x 10⁻¹⁰</td>
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Table 6 Comparison of crack growth values from DCPD technique and optical microscopy from crack growth experiments

<table>
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<tr>
<th>Specimen</th>
<th>Temp (°C)</th>
<th>Environment</th>
<th>pH</th>
<th>Salt Conc. (g/L)</th>
<th>Crack Growth DCPD (μm)</th>
<th>Crack Growth Optical Microscopy (μm)</th>
<th>Difference (%)</th>
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</table>

4 Conclusions
The average crack growth rates of all the conducted experiments are summarized in Table 5, and their comparison of crack growth measurement using DCPD technique and optical microscopy are displayed in Table 6.

Based on the conducted experiments, it can be concluded that:

1. From the experiments using SS304H at 22, 37 and 60 °C, an activation energy of 60.9 kJ/mol is obtained indicating that hydrogen diffusion controls crack growth in austenitic stainless steels.
2. Temperature plays a role in the hydrogen transport to the crack tip for crack initiation and crack growth.
3. The threshold stress intensity factor (K_{ISC}) of sensitized SS304H under substitute ocean water at 37 °C is 15 MPa m^{1/2}, and J_{ISC} is 1023.75 J/m².
4. Reducing carbon concentration increases the corrosion resistance and thus, lowering the crack growth rate.

5. Increasing salt concentration does not increase the crack growth rate (6.88 vs 6.26 mm/yr); therefore salt concentration does not affect the crack growth rate.

6. However, increasing salt concentration makes the cracks initiate earlier (27.5 vs 17.59 hrs); thus, salt concentration affects crack initiation where the higher the salt concentration, the faster the crack initiation.

7. The average crack growth rate in MgCl₂ brine is not greater than that in substitute ocean water environment (1.017x10⁻⁹ ± 1.052x10⁻¹⁰ vs 1.580x10⁻⁹ ± 2.593x10⁻¹⁰ m/s at 60 °C). Therefore, the higher chlorine content in MgCl₂ brine is suggested to be more aggressive than substitute ocean water or NaCl environment as reported in literature [23].

   a. Speidel [23] claimed that the higher chlorine content in MgCl₂ brine than that in NaCl is responsible for higher crack growth rate in MgCl₂ than in NaCl which is proven not to be true in the above experiments.

   b. Crack growth rates are strongly dependent on temperature while are essentially insensitive to the concentration.

8. DCPD technique is suitable for monitoring crack growth during SCC experiments.

9. Microstructural characterization after the experiments for the sensitized specimens indicate that cracks propagate intergranularly which is believed to be due to the chromium depletion along the grain boundaries by forming carbides (M₂₃C₆).

5 **Future Work**

Crack growth experiments on sensitized SS304L under substitute water at varied temperatures such as at 60 °C combined with the completed experiments at 21 and 38 °C will enable a determination of the activation energy for crack propagation to compare with that obtained for sensitized SS304H (60.9 kJ/mole). For $J_{IC}$ experiments, other specimens such as side-grooved might be helpful to obtain $J$-R resistance [11] and $J_{ISCC}$ on sensitized stainless steel.

6 **Acknowledgements**

We would like to thank Dr. Scott Gordon from Colorado School of Mines for providing the SS304 plates, Mr. Chris Sanford of NCSU for fabricating the WOL specimens. Special thanks are to Dr. Harvey West of NCSU for assistance during fatigue pre-crack experiments and the use of the fatigue machine and microscopes. We also would like to extend our appreciation to Prof. Zeev
Shayer from Colorado School of Mines and Dr. Charles Bryan from Sandia National Laboratory for the discussions about the experiments.

7 References
21. Lake Products Company LLC, “Sea Salt,” ASTM D1141-52 Formula a, Table 1, Sec. 4.


### 8a Conference Presentations and Publications


### 8b Publications


Chapter 10
Synchrotron X-ray Tomography Study of 304 Stainless Steel Cracks

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1. Generalities on Synchrotron x-ray tomography and its application to stress corrosion cracking

1.1 Absorption x-ray tomography

Tomography in its most general sense is the generation of a three-dimensional image by analyzing several transmission radiographic projections taken of a specimen at different angles. In a typical X-ray tomography experiment (as shown in Figure 1), a sample is rotated through 180° around an axis perpendicular to the parallel x-ray beam. The transmitted signal is recorded at regular angular interval using a scintillator, magnification optics and CCD camera. The response from each row of pixels as a function of sample rotation angle is called a sinogram. The 2D cross-section is then reconstructed from the sinogram using filtered back-projection algorithms, and the 3D volume is obtained by stacking 2D cross-sections. Element of the 3D reconstruction are called voxels, i.e. volume pixels. Prior to the reconstruction, each projection is corrected by two factors: the noise generated by the detector electronics in the absence of an x-ray beam, and the noise resulting by heterogeneities in the incident x-ray profile.

In the 2D cross-sections as well as in the 3D reconstruction, level of greys in the images are related to the local absorption coefficient in sample: the brighter the pixel (or voxel), the higher the absorption coefficient. For instance, in medical x-ray analyses, only bones are visible because they have a higher absorption coefficient compared to the soft tissues. In material science, phase contrast may appear due to the difference in the absorption coefficient, and pores, holes or cracks are easily imaged.

![Figure 1: Principle of x-ray tomography [1]](image-url)
In the process of the tomography reconstruction, the 2-D images are then put together by overlapping sample volumes (layer-1 and layer-2) that are matched based on image registration. Image registration procedure is based on feature detection, feature matching, mapping function design, and image transformation and resampling [1]. From the series of 2-D images, a 3-D representation of the sample can be obtained using image processing programs like Avizo©. For studying cracks in materials, differences in phase contrast between the crack and material can be exploited to extract information on the crack itself.

Such X-ray tomography is useful to understand better the crack propagation mechanisms especially when done in-situ. For instance, In-situ stress corrosion cracking of a 7075 aluminum was performed on the 2-BM beamline in APS [2]. The test was conducted at a relative humidity of 95%. Thanks to this experiment, the author showed that the cracks, which seem to be discontinuous when observed at the sample sides are actually connected when looking at them in the thickness (Figure 2).

![Figure 2: (a) and (b) are 2D slices of the sides of the specimen showing the discontinuous cracks (crack jump), (c) and (d) are the 3D reconstructions of part of the crack showing that the discontinuous crack at the surface are actually connected in 3D. From [2]](image)

The crack growth rate $\frac{da}{dt}$ was measured using both 2D slices and 3D reconstruction (Figure 3). As a result, the crack growth rate has a significant amount of variability when surface crack lengths were used for the measurement compared to the growth rate when the average crack length through thickness was used. Moreover, the large deviation in the surface crack lengths resulted in significant differences in stress intensity factor $K$. Thus, in-situ SCC experiment using x-ray tomography allowed to better understand the mechanism of SCC, as well as a more thorough determination of the crack growth rate.
1.2 Diffraction data information

X-ray diffraction is also used in our experiments to identify where and when corrosion products start to form and the microstructure of the corrosion products. It is also useful to identify phase changes from austenite to martensite due to deformation which are possible in metastable 304 SS. Assessing potential phase transformation during the experiment is important as one way cracks can resist growth is through phase transformation [2]. The crack tip may provide the stresses and strains needed for the deformation induced phase transformation [2]. As the crack grows, the transformed material may stay at the crack wake [2] and the larger volume of the new phase may provide a closure stress that resists crack growth [2]. Hence diffraction data was also collected throughout our experiments.

1.3 High energy diffraction microscopy (HEDM)

The second way x-ray diffraction was used is this project was to perform High-Energy Diffraction Microscopy (HEDM) to image and characterize the shape and crystallographic direction of the grains surrounding the crack [3]. High-energy diffraction microscopy was developed at the 1-ID beamline of the APS, the beam line used in our experiments. This powerful method can allow the determination of the grain structure and grain orientation of a polycrystalline material (near-field HEDM) and the

Figure 3: Crack growth rate measurement from average of the crack lengths (2D) and average of the crack length through thickness (3D). From [2]
determination of the stress field within each grain (far-field HEDM). The following section will just cover the bases of these techniques and more information can be found in references [3, 4].

The near-field HEDM consists of the same set-up as the one described above, but with several others detectors located at a certain distance of the sample and a planar x-rays beam. If the beam illuminates a sufficiently small number of grains, diffraction spots generated by individual grains can be isolated and imaged. With increasing the sample-detector distance, the diffracted beam will deviate more and more from the incident beam, as shown in Figure 5. Then, the spots (Figure 5) at different angles corresponding of a single grain are identified and the whole polycrystalline material is reconstructed. Moreover, this technique allows to determine the crystal orientation of each diffracted grain.

Figure 4: Schematic of the mapping measurement (from [3])
Figure 5: Grain diffraction spots of a polycrystalline material at different sample-detector distances $L$, where $L_1 < L_2 < L_3$. The scattering angle increases with the distance $L$.

An equivalent polycrystalline mapping technique was used to determine the effect of orientation of grain boundaries on intergranular SCC of a 302 stainless steel in a solution of potassium tetrathionate [5]. As a result, shown in Figure 6, the authors showed that the crack bridges, i.e. grain boundaries that are not sensitive to intergranular SCC, corresponds to low angles boundaries ($\Sigma 1$).

Figure 6: Combined used of DCT and CT data to identify crack-bridging boundaries structure, (a) cracks obtained from CT data are shown in black and compared with DCT data of 3D grain shapes, (b) 2D section of the grain boundaries and the crack path. Yellow boundaries: $\Sigma 1$, red boundaries: $\Sigma 3$, blue boundaries: $\Sigma 9$, purple boundaries: $\Sigma < 29$. From [5].

Far-field HEDM uses the same set-up as the near-field HEDM, with the exception that the detector is placed even farther from the specimen, which improves the angular resolution of the diffraction pattern and thus provide high elastic strain sensitivity. An example of results using this technique is shown in Figure 7. While there is no report in the literature of this method used during in-situ SCC, one can imagine
that it could be useful to determine the deformation-induced martensite transformation ahead of the crack tip due to local plasticity during SCC experiment.

![Image of a crack and plastic zone]

*Figure 7: The upper figure shows the absorption reconstruction of a crack, while the bottom figure shows the plastic zone resulting from the crack.*

These techniques were used in our in-situ experiments, but the large amount of data analysis required is not completed yet.

**2. Preliminary use of X-ray microtomography to compare with other NDT techniques used in this overall project**

In an attempt to evaluate the capabilities of several NDT tools that could eventually be deployed in the field to image SCC in stainless steel canisters, one same small 304 SS Compression Washer Sample with two cracks of mm-scale sizes was subjected to an extensive NDT program including NRUS technique, Ultrasonic C-scans, Vibro-thermography and LEGIT (all described elsewhere in this final report) and to Synchrotron X-ray microtomography as described in part 1.1. The X-ray microtomography was to serve as “control” or reference as it was expected to result in the most accurate representation of the cracks. We report here only the X-ray microtomography characterization of that crack, the results of the other methods can be found elsewhere and in the publication [4]

**2.1 Sample description:**

The multiple crevice assembly (MCA) method described in ASTM G4829 and previous studies [5-7] was adopted to study the crevice corrosion and stress corrosion cracking behavior of type 304-09A stainless steel. The sample used in this study is shown in Figure 8. The 304-09A compression washer specimen
(50×25×1.4mm) was fabricated from a wrought plate, with a through-hole geometry (6.8-mm diameter) in the center of the specimen (Figure 9b). The test surfaces of the MCA specimen were ground with 600-grit, wet silicon carbide (SiC) paper and ultrasonically cleaned with methanol for a period of 10 minutes before the test. A mixture of NaCl and KCl (50:50) salts were deposited on the specimen surface via an airbrush with a methanol carrier (6 passes). The deposition density was measured as 99.1 ug/cm² with a quartz crystal microbalance (QCM) during deposition. Once deposited, the polytetrafluoroethylene (PTFE) tape covered ceramic crevice former was used to form the crevices. Each crevice former had 12 crevice contacts and the area of each crevice contact was 0.06 cm². The PTFE tape was standard military-grade thread sealant tape with an initial thickness of 76 µm. The crevice former is shown in Figure 9a. The specimen and two crevice formers were assembled with two grade 2 titanium bolts, nuts and washers, with an applied torque of 7.91 Nm (70 in-lbs). The titanium bolts, nuts and washers were electrically isolated from the specimen with the PTFE tape. Fig. 9b shows the MCA assembly with two crevice formers. The sample was then exposed to a 105 °C environment with a dew point of 95 °C for 100 days.

Figure 8: Photograph of the sample used in the comparative study

Figure 9: (a) Ceramic crevice former, and (b) the multiple crevice assembly.
Optical observation of the crack on sample surface only show part of the whole crack along the radial direction of the hole (Figure 10). The surface crack start to appear on the specimen surface at distance of 463 µm away from the edge of the hole. Under optical microscope, the crack also appears at the middle region of the edge of the hole. Several pitting sites are found along the crack path, and more pits are found at other regions on the specimen surface. Large corrosion areas are found at the crevice contact regions. The corrosion area at the top left in Figure 10 is a small part of the crevice contact region.

An enlarged view of the surface crack with a total length of 830 µm is shown in Figure 11. Pitting sites are indicated with arrows. There are several pitting sites along the crack path. Figure 11a shows two pits that are connected by the surface crack on the lower left side. Corrosion products are found around these pits. Two large crack deviation regions (Figure 11b and c) and several small crack jumps (Figure 12) are also found along the crack path; cracks in these regions are disconnected on the specimen surface under optical observation. The crack appears to originate from surface locations (pitting sites).
Figure 11: Enlarged view of the surface crack, pitting sites and crack deviation regions. (A) Two large pitting sites along the crack path and corrosion products around the pits; (B-C) two large crack deviation regions along crack path.

Figure 12: 5. a)-d) Small crack jumps along the crack path on sample surface.
2.2. X-ray microtomography:

The microtomography experiment was conducted at the high-energy synchrotron beamline 1-ID-E at the Advanced Photon Source (APS), ANL, with a beam size of 2.1×1.3 mm. Measurements were collected with a monochromatic synchrotron X-ray beam at an energy of 90.55 keV. The specimen was mounted on a rotational stage that enabled the specimen to be rotated through a continuous 360° range with radiography collections 0.2° intervals along the rotation axis. The sample stage and detector were carefully calibrated to yield pixels rows perpendicular to the rotation axis of the sample, which facilitates reconstruction. This series of projections was reconstructed with a filtered back projection algorithm to obtain a dataset of a 3D isotropic voxels (size 1×1×1µm) representing voxel-average X-ray linear absorption coefficient. For the full crack, two vertical sample volumes were stacked.

Indeed, since the sample volume containing the full size of the crack cannot be included in one tomographic scan, two groups of tomography datasets (with partial overlapping) containing partial of the same crack were measured. Figure 13a is a schematic drawing of the SS304-09A compression washer with a through-hole geometry which shows two cracks. Figure 13b shows the 3D iso-surface rendering of two layers (layer-1 and layer-2) of the crack on the top of the hole. These 3D image datasets with partial overlapping are then matched based on image registration to form a larger sample volume containing the full crack.

![Diagram of SS304-09A compression washer with cracks](image)

**Figure**: Tomographic scan of crack in SS304-09A compression washer. (a) Schematic drawing of a SS304-09A compression washer with a through-hole geometry (6.8mm diameter) and two cracks. (b) 3D iso-surface rendering of two tomographic datasets (with partial overlapping) of the same crack. (c) Projection of layer-1 onto the YZ-plane. The unit in all axes is µm.
**Image filtering, registration and volume rendering:** Prior to the image registration, a pre-treatment of the 3D tomography data to remove the artefacts was required. As shown on the 2D slice (XY-plane) in Figure 14b, there are many bright horizontal lines, which cross the crack region. Those bright horizontal lines on the 2D slices are horizontal planes on XY-planes when observed on 3D volume rendering, as shown in Figure 14a. Due to the large width (25mm) of the specimen, X-rays are fully absorbed for a range of angles as the thick direction aligns with the beam direction. Consequently, reconstruction of the tomographic data results in artefacts that appear as bright horizontal lines (cross-hatched shading in Figure 14b).

A filter module based on fast Fourier transform algorithm is used to remove these artefacts on the 2D slices. Figure 14c shows the slice after performing filtering to the slice shown in Figure 14b. After removing artefacts on the reconstructed 3D tomography datasets, overlapping sample volumes (layer-1 and layer-2) are matched based on image registration. Image registration procedure is based on feature detection, feature matching, mapping function design, and image transformation and resampling [22]. Crack features are used to align the two volume elements to reconstruct the entire crack geometry.

![Figure 14: 3D image filtering. (a) 3D volume rendering of the crack (layer-1) before image filtering. The red dash rectangle indicates the region with artefacts. (b) Ortho slice (slice 1020 in XY-plane) before filtering, and (c) the same slice obtained by Fourier transform filtering to remove stripes (artefacts) in the horizontal direction in B.](image-url)
Visualizing the crack is achieved by thresholding the linear absorption coefficient (LAC) for each voxel [18]. Accurately extracting the whole crack volume however depends on the choice of threshold in the 16-bit grayscale image; the threshold value selected will determine the interface position between the crack and the matrix [16]. For this investigation, an intermediate value was taken corresponding to the valley between the air and steel absorption peaks in the 16-bit LAC distribution. Finally, a ‘seed’ growth technique for voxel continuity was applied to eliminate noise, to create a fully connected 3D voxel set representing the crack and interface. Those voxels that belong to the crack are set at fully opaque, whereas the voxels belonging to the matrix are set at fully transparent.

**3D Visualization and Analysis of the Crack:** The full 3D crack reconstruction yields a 3D volume (Figure 15) rendering of the crack with multiple crack branches. The volume rendering of the crack was aligned to be parallel to the YZ-plane. The main crack volume is labelled with blue colour. Crack branches are labelled with different colours in order to differentiate them from the main crack. The extracted crack volume is projected onto YZ-plane for both positive X (Figure 15b) and negative X (Figure 15d) direction, which is perpendicular to the loading direction. Optical image (Figure 15c) is used to compare the surface crack with the 3D crack morphology. The corrosion pits (1-2) and crack jumps (3-4) are matched between optical surface observation (Fig. 15c) and 3D tomography results (Fig. 15b-d). (1) and (5) indicates the edge of the crack appears on the sample surface.

![Figure 15: (a) 3D volume rendering of the crack with multiple crack branches. A projection of the crack volume onto YZ-plane on (b) positive X direction and (d) negative X direction. a - d indicate five different crack branches labelled with different colours. The unit in each axis is µm. (c) Microscope image showing](image-url)
As expected it was found that there is a tradeoff between the ease of implementation (and applicability in the field) and level of detail that can be obtained from the technique [4]. For instance, a detailed 3D image of the crack could be obtained with X-ray tomography, but this technique cannot be deployed in the field. On the other hand, NRUS was shown to be a powerful and easy to implement tool for detecting the presence of one or multiple cracks but cannot be used to locate or image the cracks. Ultrasonic C-scans could image the cracks and their penetration depth. However, the probe needs to be coupled to the structure with a fluid, which would require some engineering design if this technique were to be deployed inside the concrete overpack. More importantly, C-scans cannot differentiate a crack from a notch or surface scratch because of the physics involved in the imaging processing (echoing of the incident ultrasonic waves). Vibro-thermography and LEGIT provide very similar images of the cracks and are transparent to the presence of surface scratches. These two techniques are based on the same physical mechanism, namely, the clapping (opening and closing) of the cracks interacting with the incident ultrasonic waves. Vibro-thermography exploits temperature changes whereas LEGIT exploits the generation of harmonics by the cracks for detection and wave-field discontinuities at the crack for imaging. Vibro-thermography cannot be currently deployed in the field because of the geometrical constraints in the concrete overpack. The infrared camera would have to be miniaturized and shielded from the radiations for the technology to be deployable. However, LEGIT could be deployed with some changes to the setup and equipment.

3. In Situ SCC Experiments using Custom Tensile Machine

We (in Dr Kaoumi’s group) proposed to apply X-ray microtomography in situ during SCC experiments. The goal was to investigate the mechanisms of CISCC in different variations of 304 which include commercial 304, a high carbon 304H, and a low carbon 304L (Compositions shown in Table 1). Samples were obtained by fatigue pre-cracking 5x5x55 mm samples in air and then extracting out a 1.2x1.2x35 mm sample containing ~200 μm of pre-crack by Electrical Discharge Machining (EDM) as shown in Figure 16. Samples less than 1.8 mm thick are needed to have only one scan to contain the crack and to allow enough x-rays to pass through the sample. After evaluating the possibility of using different
variations of designs for the in situ mechanical testing device, one design was chosen and is shown in Figure 17. The left most picture represents a diagram of the in situ tensile machine. The machine itself is composed of a motor to induce a load, a load cell to measure the load, a kapton chamber to hold in the marine environment, a K-type thermocouple to measure temperature, and a relative humidity sensor. The design was good for x-ray tomography because the kapton chamber was relatively transparent to x-rays and the two-pillar setup provided stability compared to a single pillar. Slits in the pillars enabled for x-ray images to be taken at more angles to the point where reconstruction can still be completed. The tensile machine was placed on a rotating stage to allow 360° rotation relative to the stationary x-ray beam as depicted in the right most picture of Figure 17. For the heating source, the first set of experiments that were completed in October 2017 used a heating gun that was stationary relative to the rotating stage. The disadvantage of this method was there was an oscillation in temperature by about 15°C which led to a stress oscillation of about 40 MPa due to expansion and compression with temperature. The cause of the oscillation was found to be due to the rotation of the tensile stage relative to the heating gun. The pillars would partially block the heating gun and cause the decrease in temperature. The second set of experiments that was performed in June 2018 fixed this problem by mounting two infrared heaters onto the tensile machine for constant heat application.

Table 1: Chemical Composition (wt%) of 304, 304L, and 304H

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>0.0216</td>
<td>0.198</td>
<td>18.3105</td>
<td>0.3915</td>
<td>1.828</td>
<td>0.2855</td>
<td>0.0889</td>
<td>8.1125</td>
<td>0.325</td>
<td>0.001</td>
<td>0.251</td>
<td>Balance</td>
</tr>
<tr>
<td>304H</td>
<td>0.0418</td>
<td>0.1345</td>
<td>18.193</td>
<td>0.4005</td>
<td>1.7495</td>
<td>0.2985</td>
<td>0.0844</td>
<td>8.0725</td>
<td>0.0335</td>
<td>0.001</td>
<td>0.293</td>
<td>Balance</td>
</tr>
<tr>
<td>304</td>
<td>0.022</td>
<td>0.15</td>
<td>18.1</td>
<td>0.45</td>
<td>1.68</td>
<td>0.30</td>
<td>0.09</td>
<td>8.4</td>
<td>0.037</td>
<td>0.025</td>
<td>0.40</td>
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</tr>
</tbody>
</table>
Figure 16: Fatigue Pre-Cracking Samples in Air to Extract Small Pre-Cracked Samples

Figure 17: In Situ SCC Design for Tomography and Diffraction Scans
To induce CISCC, a drop of concentrated MgCl₂ solution was added to the crack before the start of the experiment. Research has shown that MgCl₂ is one of the most harmful salts found in sea salts to stainless steels. To control the relative humidity, a drop of water was added to the cell via a syringe to keep the relative humidity above a critical level. The parameters used for the October 2017 experiments are shown in Table 2. For the stress level, the desire was to get close to the yield strength of the material of the unfractured portion of the sample. After the test, the tomography scans provided a more accurate dimensions of the sample and it was determined that the actual true stress was higher for all samples, especially the commercial 304 sample. The experiment was run in fixed extension mode meaning that the sample was put under the desired stress initially and the position was fix over time. The stress on the sample decreased over time due to crack propagation reliving stress. The temperature was set at 80°C which corresponds to the temperatures that the canisters can reach. A relative humidity was set to 55-65% which is above the critical level for the deliquescence of MgCl₂. Three days of beam time on the 1-ID-E beamline was obtained and experiments duration were dictated by this time.

Table 2: Experimental Conditions for October 2017 Experiment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Desired True Stress (MPa)</th>
<th>Actual True Stress (MPa)</th>
<th>Temperature (°C)</th>
<th>Humidity (%)</th>
<th>Experiment Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>440</td>
<td>534</td>
<td>80</td>
<td>55-65</td>
<td>15.8</td>
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<tr>
<td>304H</td>
<td>300</td>
<td>324</td>
<td>80</td>
<td>55-65</td>
<td>21.7</td>
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<tr>
<td>304L</td>
<td>280</td>
<td>308</td>
<td>80</td>
<td>55-65</td>
<td>13.8</td>
</tr>
</tbody>
</table>

The results of this experiment (shown in the next sections) were used to set the experimental conditions used for the second set of experiments in June 2018. Table 3 shows the experimental conditions used for the second set of experiments. The results from the October 2017 sample indicted that the 304 sample underwent SCC while the other two samples might not have had enough stress to induce more cracking. As a result, the stresses on the 304H and 304L sample was increased. The stress for the 304 sample was reduced to see if cracking rates were changed at a lower stress. The experiment was also run in constant load so that the stress intensity would increase with crack growth.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Desired True Stress (MPa)</th>
<th>Actual True Stress (MPa)</th>
<th>Temperature (°C)</th>
<th>Humidity (%)</th>
<th>Experiment Time (hours)</th>
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<tbody>
<tr>
<td>304</td>
<td>400</td>
<td>392.1</td>
<td>80</td>
<td>55-65</td>
<td>20.1</td>
</tr>
<tr>
<td>304H</td>
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<td>20.7</td>
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<tr>
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<td>330.2</td>
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<td>55-65</td>
<td>17.8</td>
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<tr>
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<td>350</td>
<td>336.9</td>
<td>80</td>
<td>55-65</td>
<td>15.3</td>
</tr>
</tbody>
</table>

### 4. Reconstruction of Tomography from In Situ Experiments

After completing the experiments, the computer clusters at APS was used to complete the reconstruction and produce a series of 2-D slices. The 2-D slices were constructed into 3-D representations of the crack using a program called Avizo®. The program was used to extract out just the crack so that accurate representations of the cracks could be analyzed. Because the crack has a different phase contrast, it can be extracted; however, micro voids in the sample have the same contrast and are extracted as well. In some cases, the micro voids were removed because too many of them can obscure the crack. The tomography from the October 2017 experiment over time for the 304 sample with micro voids removed is shown in Figure 18. From the figure, it is clear that a branching structure started to form around 6.3 hrs into the experiment and grew larger over time. Figure 19 shows the final 304 scans at different angles to better see the morphology of the cracks. As seen in the figure, the branching cracking seems to be limited more towards the surface whereas the middle does not have much branching.
The next sample that was analyzed was the 304H sample from the October 2017 set of experiments. The tomography over time are shown in Figure 20. Unlike the 304 sample, the 304H sample contained vertical cracks around the crack tip. It should be noted that this sample did not contain many micro voids, so they
were not removed. The height of the vertical cracks is around 100 μm. Different angles of the final scan for the 304H sample is shown in Figure 21. The vertical cracks appear to be more concentrated in the center of the crack tip with a few near the edges. Figure 22 and Figure 23 show the tomography over time and the final tomography at different angles for the 304L sample from the October 2017 set of experiments, respectively. The 304L results show that the sample also contains vertical cracks like the 304H sample, but the vertical cracks are along the crack wake as well as the crack tip. Additionally, the 304L vertical cracks do not appear to be as concentrated around the center of the crack tip.

Figure 20: Tomography of the 304H Sample over Time from the October 2017 Experiments (units in microns)
Figure 21: Final Scan for 304H Sample at Different Angles from October 2017 Experiments (units in micron)

Figure 22: Tomographs of the 304L Sample over Time from the October 2017 Experiments (units in microns)
Compared to the experiments done in October 2017, the experiments done in June 2018 did not have much crack growth; this was believed to be due to a couple of factors. The first of which is that the salt was not well deposited on the samples. A drop of concentrated salt solution was applied to the crack mouth and then wiped off with a Kimtech wipe. Salt was only desired in the crack itself to ensure that cracking would only come from the crack and not pits that might have formed on the surface if salt solution was left on it. Additionally, the stress intensity for the samples might still have been too low to induce chlorine induced stress corrosion cracking. These observations helped motivate the next round of experiments which are shown in Table 4. For the 304H and 304L samples, a larger stress intensity (K) was used to induce cracking. For a 304 and 304L sample, a lower temperature of 50 °C was used to see if there was any temperature effect on the crack growth rate. One 304 sample was put at a stress intensity similar to the 304H and 304L samples that gave vertical cracks to see if vertical cracks would form.
Table 4: October 2019 Experimental Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress (MPa)</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Time (hrs)</th>
<th>K Initially</th>
<th>Goal</th>
</tr>
</thead>
<tbody>
<tr>
<td>304H</td>
<td>Based on K</td>
<td>80</td>
<td>55-65</td>
<td>12</td>
<td>45</td>
<td>To cause cracking at a high K</td>
</tr>
<tr>
<td>304H</td>
<td>Based on K</td>
<td>80</td>
<td>55-65</td>
<td>12</td>
<td>40</td>
<td>To see if cracking was still evident at a lower K</td>
</tr>
<tr>
<td>304</td>
<td>Based on K</td>
<td>50</td>
<td>55-65</td>
<td>8.5</td>
<td>40</td>
<td>To see if there was a temperature effect at the same K</td>
</tr>
<tr>
<td>304L</td>
<td>Based on K</td>
<td>80</td>
<td>55-65</td>
<td>12</td>
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<td>To cause cracking at a high K</td>
</tr>
<tr>
<td>304</td>
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<td>13.5</td>
<td>20</td>
<td>To see if vertical cracks would form</td>
</tr>
<tr>
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<td>Based on K</td>
<td>50</td>
<td>55-65</td>
<td>12</td>
<td>40</td>
<td>To see if there was a temperature effect at the same K</td>
</tr>
</tbody>
</table>

5. Post-Experiment Analysis and Stress Intensity Analysis

To help understand the cracking phenomena for both experiments, post-experiment characterization and stress intensity analysis were conducted. The post-experiment characterization included Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS), Scanning Transmission Electron Microscopy (S/TEM), and the synchrotron x-ray diffraction data. SEM and EDS maps of the 304 sample from the October 2017 experiments are shown in Figure 24. The chemical maps show that around the crack tip, there appears to be oxygen as well as magnesium and chlorine. The presence of the salts at the main crack tip indicates that salt was able to migrate in the crack to cause CISCC. The chemical maps corresponding to the 304 sample that was apart of the June 2018 experiments is shown in Figure 25. For the June 2018 304 sample, there appears to be spots of chlorine and magnesium, but they do not appear to be at the crack tip. EDS maps of the other June 2018 samples showed a similar trend. This indicates that the salts may have not been able to penetrate into the crack tip region from the beginning of the experiment. The salt solution might have not been applied well enough to induce ICSCC. Interestingly, although ICSCC might not have occurred, an enrichment of copper can be seen on the EDS maps and appeared in other June 2018 experiments. Because SCC was not really
observed in the June 2018 samples, most of the analysis was done on the October 2017 samples which cracking was observed.

Figure 24: SEM and EDS Maps of 304 Sample from October 2017

Since the 304-sample appeared to crack the most, STEM and TEM analysis were conducted to observe the microstructure around the crack tip as well at the crack. Two TEM lift outs were extracted using Focused Ion Beam (FIB) techniques. The first lift out was taken in the plastic zone as shown in Figure 26. The corresponding TEM lift out is shown in Figure 27 along with a zoomed in area and a
diffraction pattern. From the low magnification TEM image, there appears to be damage in this region with the presence of bands. Upon taking a diffraction pattern of the bands, spots corresponding to alpha prime martensite’s (110) family of reflections appears. This region had developed deformation induced martensite as a result of the stress and strains in the plastic zone. To see the effect of phase transformation on the SCC of the samples, the synchrotron x-ray diffraction data was analyzed and is discussed later. The next part of the sample that was observed was the crack to try and characterize the corrosion layer that might have formed inside the crack. The location of the FIB lift out is shown in Figure 28. Chemical maps that were obtained in STEM mode using ChemiSTEM are evident in Figure 29. From the chemical maps, the area rich in magnesium and chlorine can be seen. Interestingly, the chlorine does not overlap completely with the magnesium meaning that the chlorine might have reacted with something. Additionally, like the SEM EDS maps of the June 2018 samples, areas rich in copper are evident. Moreover, areas around the crack also appear to be slightly enriched in chromium and nickel. To determine what structures and compounds have formed on the inside of the crack, Selected Area Electron Diffraction (SAED) was conducted and is shown in Figure 30. The diffraction pattern shows ring like structures meaning that the two area are nanocrystalline. Furthermore, the two diffraction patterns are different in terms of the radius of the rings. Analyzing the ring radius and converting it to a d-spacing and using the chemical maps revealed that the towards the outside of the crack (Bottom Diffraction Pattern in Figure 30) most likely belongs to chromium (II) chloride while the inner region (Top Diffraction Pattern in Figure 30) most likely belongs to nickel (II) chloride. As for the copper enrichment, this could be interpreted in the light of results reported in [8] for experiments done on 304 in a sulfuric acid solution with the addition of sodium chloride using atomic emission spectroscopy; the authors reported the dissolution of other elements such as iron, chromium, and nickel into solution but found that copper ended dealloying on the surface due to the fact the copper can serve as a better cathode compared to stainless steel [8].
Figure 26: Area of First Liftout in Plastic Zone of 304 Sample from October 2017

Figure 27: TEM Liftout and Selected Area Diffraction Pattern of 304 October 2017 Sample near Plastic Zone
Figure 28: Area of Second Lift out in Branching Crack of 304 Sample from October 2017

Figure 29: ChemiSTEM Maps of Crack Region in 304 Sample from October of 2017
Since martensitic phase transformation was evident in the 304 sample under TEM, the role of martensite formation was analyzed using the data from the synchrotron x-ray diffraction. Using the x-ray diffraction data obtained from the experiment at APS performed in October 2017, the phase fractions can be calculated. For the diffraction scans, a beam size of 1.2x0.1 mm was used and was taken above the crack, at the crack, and below the crack as is evident in Figure 31. The raw data was treated using a matlab code provided by the beamline staff at 1-ID that was used to integrate over the entire ring pattern and create a GSASII readable file. After treatment, each scan was observed in GSASII like the one shown in Figure 32 for the commercial 304 sample before loading. To determine the phase fractions, the three main phases (γ-Fe, α’-Fe, and ε-Fe) were uploaded into GSASII and the program was used to try and calculate the phase fractions by altering parameters like the lattice parameter, microstrain, texture, and phase fraction. Although GSASII is a powerful tool to determine phase fractions, the program had issues with trying to fit the smaller epsilon iron peaks. To get around the problem, an ASTM standard was used to determine phase fractions [9]. The process involves obtaining the integrated intensity under the curve and then using factors like the multiplicity, the Debye-Waller factor, the atomic scattering factor, and the Lorentz polarization factor to normalize each peak. The integrated intensities of each phase’s peaks are divided by their respective normalization constants and the average is taken. The averages can then be used to determine the phase fractions. The normalization constant formula is shown in the formula followed by the formula used to calculate the phase fractions.
Figure 31: Location of X-ray Diffraction Scans Above the Crack, at the Crack, and Below the Crack (units in μm)

Figure 32: X-ray Diffraction Integrated Spectrum for Commercial 304 before Loading
\[ R = \frac{|F|^2 pLP e^{-2M}}{v^2} \]

- \(|F|^2\): Structure Factor
- \(p\): Multiplicity
- \(LP\): Lorentz Polarization Factor
- \(e^{-2M}\): Debye-Waller Factor
- \(v\): Volume of Unit Cell

\[ V_i = \frac{1}{n} \frac{\sum_{j=1}^{n} I_j^i R_i}{\sum_{j=1}^{n} I_j^y R_y + \sum_{j=1}^{n} I_j^{\alpha\alpha} R^{\alpha\alpha} + \sum_{j=1}^{n} I_j^{\epsilon\epsilon} R^{\epsilon\epsilon}} \]

The constants used to obtain the normalization factor can be found in [10]. The integrated intensities were obtained by fitting the curves with Gaussian and Lorentzian functions using GSASII. To see how the initial martensite phase fraction might have affected the cracking, the phase fractions of 304, 304H, and 304L were calculated before loading but after fatigue pre-cracking. The samples were then compared to a reference sample of 304H to determine how fatigue could have influenced the results. Because the scans were conducted above the crack, at the crack, and below the crack, the phase fractions were calculated at each and then they were all used to determine the phase fraction of the overall area around the crack. The beam size used was 1.2x0.1 mm to correspond to the sample width and the height of the scanned regions. The results from the standard 304H sample is shown Table 5. The intensity of the scan was low due to data only being obtained in the loading and transverse direction that was used in another study. As a result, the epsilon peaks were hard to distinguish and are represented as zero in the table. Table 6 and Table 7 show the phase fractions for 304, 304H, and 304L from October 2017 before the experiment (after fatigue) and after the experiment. Since the standard sample was 304H, only the 304H sample can truly be compared and the results show that fatigue most likely induced the formation of some martensite. Comparing before and after the experiment of all the samples, the 304 and 304L samples both increased slightly in martensite while the 304H sample decreased by a negligible amount. These results indicated that in fact the vertical
cracks observed in the 304H and 304L samples were not due to deformation induced martensitic transformation happening during the in-situ experiments. In fact, it is hypothesized that a too low stress intensity factor was most likely the reason why the SCC did not occur in the 304H and 304L and that vertical cracking along martensitic laths already pre-existing in the precracked sample was thus the preferred way of stress relief.

Table 5: Standard 304H Sample Phase Fractions

<table>
<thead>
<tr>
<th></th>
<th>γ-Fe</th>
<th>α'-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transverse</td>
<td>96.31</td>
<td>3.68</td>
</tr>
<tr>
<td>Loading</td>
<td>98.69</td>
<td>1.3</td>
</tr>
<tr>
<td>Average</td>
<td>97.97</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Table 6: Phase Fractions before Loading for October 2017 Experiments

<table>
<thead>
<tr>
<th></th>
<th>304</th>
<th>304H</th>
<th>304L</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Fe</td>
<td>α'-Fe</td>
<td>ε-Fe</td>
<td>γ-Fe</td>
</tr>
<tr>
<td>Above Crack</td>
<td>93.43</td>
<td>5.7</td>
<td>0.86</td>
</tr>
<tr>
<td>At Crack</td>
<td>86.69</td>
<td>11.62</td>
<td>1.67</td>
</tr>
<tr>
<td>Below Crack</td>
<td>91.24</td>
<td>7.85</td>
<td>0.89</td>
</tr>
<tr>
<td>Total</td>
<td>91.13</td>
<td>7.81</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Table 7: Phase Fractions at the end of Experiment for October 2017 Experiments

<table>
<thead>
<tr>
<th></th>
<th>304</th>
<th>304H</th>
<th>304L</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Fe</td>
<td>α'-Fe</td>
<td>ε-Fe</td>
<td>γ-Fe</td>
</tr>
<tr>
<td>Above Crack</td>
<td>88.16</td>
<td>10.4</td>
<td>1.42</td>
</tr>
<tr>
<td>At Crack</td>
<td>94.07</td>
<td>4.65</td>
<td>1.27</td>
</tr>
<tr>
<td>Below Crack</td>
<td>88.46</td>
<td>10.1</td>
<td>1.43</td>
</tr>
<tr>
<td>Total</td>
<td>89.66</td>
<td>8.94</td>
<td>1.39</td>
</tr>
</tbody>
</table>
The last point of analysis was thus stress intensity analysis to see how it might have influenced the results. With the ability to perform tomography scans in situ, it is possible to determine the crack rate as a function of stress intensity. In order to get crack rate, the length of the crack at each scan was taken and divided by the time between scans. In terms of stress intensity factor a mathematical technique described in [11] was used to estimate the stress intensity factor for a single edge crack. The standard formula for calculating stress intensity factor is shown in Equation 1 where $K_I$ is the stress intensity factor for type I loading, $Y$ is the geometric shape factor, $\sigma$ is the far field stress and $a$ is the crack length.

\[
K_I = Y \sigma \sqrt{\pi a} \quad (1)
\]

The method used for the initial scan for 304 and all the scans for 304H and 304L utilizes a non-dimensional stress intensity factor to account for the change in the geometric factor as the crack propagates. The following two formulas were used to estimate the stress intensity factor after obtaining crack length, sample width, and far field stress [11]. The ratio of crack length to sample width in the same direction as the crack is $\alpha$ while $C_n$ and $t$ are constants [11].

\[
F_I = \frac{(1 - \alpha)^{3}K}{\sigma \sqrt{\pi a}} \quad (2)
\]

\[
F_I = 1.1215(1 - \alpha) + \alpha(1 - \alpha) \sum_{n=0}^{4} C_n a^n + 1.1215t \alpha \quad (3)
\]

In order to obtain stress intensities, crack length measurements were required. To measure the crack length, six equidistant points were taken and averaged to give average crack length as shown in Figure 33. With the crack lengths, stress intensities for each of the samples was calculated and the results are shown in Table 8. As could be seen from the tomography, the 304 sample had the largest amount of crack growth. Upon looking at the initial stress intensity among all the samples, the 304 sample started off initially with a higher stress intensity compared to the similar lower stress intensity of 304H and 304L. Additionally, the highest drop in stress intensity was found to be in the 304 sample due to the crack growth. The factor of stress intensity was further explored using finite element analysis which was conducted by our colleagues at the Colorado School of Mines (Dr. Yu’s group). The results of the finite element analysis using ABAQUS© based of the conditions of the experiments are shown in Figure 34. The results of the finite element analysis show that the 304 sample had a large area of maximum principle stress. Moreover,
the shape of it can be seen as branching. Unlike the 304 sample, the 304H and 304L samples only have a small concentrated region of the maximum principle stress. From the finite element and stress intensity analysis, it appears that CISCC might have only been observed in the 304 sample because the stress intensity was high enough ($K > K_{ISCC}$) to induce stress corrosion cracking whereas the other samples might have been too low. Although 20 MPa $m^{1/2}$ is seen in other experiment to cause stress corrosion cracking, the small size of the samples can lead to the increase of the critical stress intensities [12].

Figure 33: Example of Crack Length Measurements
Table 8: Crack Length and Stress Intensities for October 2017 Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>304H</th>
<th>304</th>
<th>304L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engineering Stress at Beginning (MPa)</td>
<td>165.5</td>
<td>209.1</td>
<td>164.9</td>
</tr>
<tr>
<td>Engineering Stress at End (MPa)</td>
<td>150.7</td>
<td>84.3</td>
<td>128.5</td>
</tr>
<tr>
<td>Average Crack Length at Beginning (um)</td>
<td>620.1</td>
<td>653.8</td>
<td>527.9</td>
</tr>
<tr>
<td>Average Crack Length at End (um)</td>
<td>694.6</td>
<td>902.3</td>
<td>561.2</td>
</tr>
<tr>
<td>Difference (um)</td>
<td>74.5</td>
<td>248.5</td>
<td>33.3</td>
</tr>
<tr>
<td>KI at Beginning</td>
<td>21.5</td>
<td>41.1</td>
<td>18.3</td>
</tr>
<tr>
<td>KI at End</td>
<td>26.6</td>
<td>3.2</td>
<td>16.1</td>
</tr>
</tbody>
</table>
The expected curve of the crack rate as a function of stress intensity is shown in Figure 35. Above the critical stress intensity for SCC, the crack rate depends on the stress intensity. The crack rate is then predicted to reach a steady state region at high stress intensities followed by a rapid increase in rate as the stress intensity reached $K_{IC}$. 

Figure 34: Results of Finite Element Analysis on October 2017 Samples
For the experiment run in October 2017, the samples were run in a constant crack opening mode so the stress intensity should decrease with time as the crack propagates. To deal with the branching cracks that form on the commercial 304 sample, stress intensities were calculated by both ignoring the length of the branches (branching on towards the edge of the samples) and also by taking the length of the branches into account. The case where branching is ignored is shown in Figure 36. From the data, the commercial 304 sample appears to be in the steady state regime and might be heading into the fracture regime. The average crack rate is shown as the red line in Figure 36. Figure 37 depicts the results when the branching length is taken into account. The results of the commercial 304 with branching do not appear to be too different to the same results when branching is ignored. The same shape and a similar average crack rate can be seen between Figure 36 and Figure 37. The crack rate as a function of stress intensity for both 304H and 304L are shown in Figure 38 and Figure 39, respectively. The 304H curve shows a slight decrease in the cracking rate with an increasing stress intensity. The data points for 304L appear to be scattered around the average but over orders of magnitude. Both the 304H and 304L do not appear to have the typical shape of the curve that is common for stress corrosion cracking.
Figure 36: Average Crack Length over Time (Left) and Crack Rate vs. Stress Intensity (Right) for Commercial 304 Sample Ignoring Branching

Figure 37: Average Crack Length over Time (Left) and Crack Rate vs. Stress Intensity (Right) for Commercial 304 Sample with Branching
6. In situ Experiments in October 2019

With the knowledge from the experiments conducted in October 2017 and June 2018, an experiment planned for October 2019 was completed. Beam time was again awarded on the 1-ID-E for in situ x-ray tomography and diffraction. A table showing the parameters, including stress intensity, is shown in Table 9 and Table 10 for the October 2017 and June 2018 experiments, respectively. The conclusion from the experiments have shown that stress intensity might be a critical factor for inducing ICSCC so the experiments that were run in October 2019 are shown in Table 11. The samples were immersed in the MgCl$_2$ solution for about 30 seconds to make sure salt gets to the crack tip to avoid not cracking like in the June 2018 experiment. To investigate the role of temperature, two of the experiments were conducted at a lower temperature of 50 °C instead of 80 °C. Additionally, a 304 sample was run at the stress intensity of 20 MPa m$^{1/2}$ to see if vertical cracks like those saw in 304H and 304L back in October 2017 would develop. The goal of the experiment would to gain better insight into the mechanisms of ICSCC and to induce ICSCC in the 304H and 304L samples. Besides the in-situ experiment, the processing of the HEDM data from the other in-situ experiment still needs to be analyzed to obtain crystallographic information about the grains around the crack. The process would involve using software’s like Paraview and DREAM.3D to reconstruct the microstructure using the diffraction data at each step.
Table 9: October 2017 Experimental Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress (MPa)</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Time (hrs)</th>
<th>K Initially</th>
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<tbody>
<tr>
<td>304L</td>
<td>280</td>
<td>80</td>
<td>55</td>
<td>13.8</td>
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<tr>
<td>304</td>
<td>440</td>
<td>80</td>
<td>55</td>
<td>15.8</td>
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<td>304H</td>
<td>270</td>
<td>80</td>
<td>55</td>
<td>13.8</td>
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</table>

Table 10: June 2018 Experimental Conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress (MPa)</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Time (hrs)</th>
<th>K Initially</th>
</tr>
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<tr>
<td>304-4</td>
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<td>55-65</td>
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<td>55-65</td>
<td>17.8</td>
<td>17.253</td>
</tr>
<tr>
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<td>80</td>
<td>55-65</td>
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<td>13.558</td>
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Table 11: Experiment for October 2019

<table>
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<tr>
<th>Sample</th>
<th>Stress (MPa)</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Time (hrs)</th>
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<td>12</td>
<td>45</td>
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</tr>
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<td>55-65</td>
<td>12</td>
<td>40</td>
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</tr>
<tr>
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<td>Based on K</td>
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<td>55-65</td>
<td>8.5</td>
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<td>To see if there was a temperature effect at the same K</td>
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<td>55-65</td>
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<td>12</td>
<td>40</td>
<td>To see if there was a temperature effect at the same K</td>
</tr>
</tbody>
</table>
7. References


