Brief Trip Report from 2015 NACE Conference on March 15–19, 2015 at Dallas, TX

1) Corrosion and Corrosion Control of Buried Piping in Nuclear Power Plants

- US Nuclear Regulatory Commission Activities Regarding Buried and Underground Piping at Nuclear Power Plants by David Alley

This work was presented by David Alley from NRC. NRC participated in the Underground Piping and Tanks Integrity Initiative to revise guidance regarding buried and underground piping related to license renewal and developing a process for the oversight of buried and underground piping activities at currently operating nuclear power plants. The process included the development of the buried piping action plan and a temporary instruction addressing inspection activities associated with buried piping. Future NRC activities associated with buried and underground piping include: (i) being active in the area of buried piping, (ii) continuing to track leaks from buried pipe, coordinate with industry groups, participate in consensus organizations and in the future, conduct another assessment of the status of the industry initiative and/or plants buried piping asset management plans.

- A Novel Pulsed Eddy Current Technology for the Inline Inspection of Internally Lined Piping

This work discussed the development of a novel dynamic pulsed eddy current system that provides the ability to measure the remaining wall thickness of carbon steel and cast iron pipe through liners. The differential pulsed eddy current peak amplitude and the decay rate of the pulsed eddy current response have been correlated to pipe remaining wall thickness. The system can be equipped to be mounted on a robotic inline inspection crawler and acquire data dynamically while the sensor is in motion. Initial applications have revealed results from robotic scanning at sensor lift-off distances of up to 15.9 mm (0.625 in) of carbon steel pipe are promising. This new technology will provide the nuclear industry with an inline inspection solution for the assessment of cement-lined and other lined piping systems.

2) Mechanisms of Localized Corrosion

Overall, crevice repassivation potential measurement using potentiodynamic-galvanostatic-potentiodynamic method has been commonly used to assess localized corrosion susceptibility.

- Localized Corrosion of Corrosion-resistant Alloys in Environments Containing Hydrogen Sulfide

The tendency of stainless steels and nickel alloys to undergo localized corrosion as a function of environmental conditions (solution composition, temperature, and pressure) has been evaluated based on the comparison of corrosion potential and repassivation potential. The potentials were measured and compared with a mechanistic model computing the

repassivation potential. The model prediction is consistent with the measured critical crevice temperature.

- The influence of pH on localized corrosion behavior of X65 (UNS K03014) carbon steel in CO_2-saturated brines

Pitting factor (PF) has been introduced as a tool for characterization of the nature of corrosion damage in the work.

- Effects of anions on the crevice corrosion behavior of copper in groundwater

University of Science and Technology Beijing conducted crevice corrosion tests of copper in simulated groundwater. But the paper didn't state if the test was performed in oxic or anoxic condition. It was found that the presences of Cl^- and SO_4^{2-} promoted the corrosion process of copper, while CO_3^{2-} exhibited a suppressive effect. When the concentration of Cl^- in solution was lower, the addition of SO_4^{2-} promoted crevice corrosion. However, when the concentration of Cl^- was higher, most of the copper corrosion occurred through active matrix dissolution outside the crevice. CO_3^{2-} caused surface passivation of the copper and had an inhibiting effect against crevice corrosion by Cl^- and SO_4^{2-}, but the protective effect depends on the concentrations of each ion. The composition of the corrosion product film inside the crevice or near the crevice month could be revealed if crevice corrosion occurred. When the reddish brown corrosion product (Cu_2O) formed inside the crevice or near the crevice month, crevice corrosion had occurred, while if no crevice corrosion occurred, the black corrosion product (CuO) was observed.

- Effect of Copper on Crevice Corrosion Inhibition of Nickel-Chromium-Molybdenum Alloy in Aggressive Conditions

Western University in Canada presented the work. The effect of Cu on the localized corrosion of Ni-Cr-Mo alloys has been investigated in hot saline solutions by comparing the behavior of alloys, Alloy 59 (UNS N06059) and C-2000 (UNS N06200), using electrochemical and surface analytical techniques. Copper did not have any measurable effect on passive film properties or on either the breakdown and repassivation potentials or the protection temperature. Galvanostatically controlled crevice corrosion experiments clearly demonstrated that copper suppressed metastable breakdown events, precursor for stable pits. Dynamic secondary ion mass spectrometry (D-SIMS) showed copper accumulated in crevice corroded locations but could not confirm any influence of copper on crevice propagation.

- Effect of thiosulfate on metastable pitting in chloride containing environment

Georgia Tech presented the work. This study explored the effect of thiosulfate on the metastable pitting of UNS S30403 in 0.6 M chloride solution. A significant decrease in the pitting potential was found in 0.6M chloride solution after 0.03M thiosulfate addition. Chronoamperometry was used to study the metastable pitting behavior of UNS S30403. Specimens were polarized at -0.1 V and 0 V vs. SCE. By analyzing the frequency and peak current distribution of the metastable pits, it was found that thiosulfate promotes both metastable pitting frequency and growth. A turning point was found on the log I_{peak} vs. cumulative frequency curve, which may correspond to the size of the pit at which reduced sulfur species start to facilitate pitting.

3) Assessment and Control of Corrosion in Reinforced Concrete Structures

- Application of electrochemical techniques in the corrosion process of rebar in the concrete

Gamry Instruments gave a brief review of electrochemical techniques used in the concrete industry. The corrosion process of rebar in the concrete with the immersion in NaCl solution was studied with Linear Polarization Resistance (LPR) technique**,** Electrochemical Frequency Modulation (EFM) and Electrochemical Impedance Spectroscopy (EIS). Polarization resistance of rebar using LPR, EFM and EIS techniques exhibits a good agreement to some degree. Analysis of EIS for rebar in the concrete was discussed. An integration of multiple electrochemical techniques into one system is practical and useful for the corrosion monitor and corrosion mechanism of rebar in the concrete.

- Material and Corrosion Evaluation of Deficient PT Grout with Enhanced Sulfate Concentrations

Florida Department of Transportation showed that high sulfate concentrations can be accumulated in deficient grouts without external sulfate sources. Enhanced corrosion can occur in deficient grout created with expired grout and excessive mix water.

- Passive Wireless Surface Acoustic Wave Sensors for Corrosion Monitoring of Steel in Concrete Structures

Wireless, passive, surface acoustic wave (SAW) corrosion sensors have been developed, built and embedded in concrete. An experimental test consisting of immersing the concrete blocks with the sensors in a salt water tank for an accelerated corrosion process was designed. These sensors are small in size, rugged, and can be embedded in concrete structures for decades and remain capable of responding to external RF interrogation pulses.

4) Corrosion in Nuclear Systems

- Effects of Metallurgical Factors and Waste Chemistry on Localized Corrosion and SCC of Hanford Radioactive Waste Tank 241 AY-102

N. Sridhar from DNVGL presented the results of ongoing studies on the effects of various waste chemistries on localized corrosion and SCC of one of the double-shell tanks, which experienced a leak of the primary tank liner. The chemistries of the waste in the annular space of AY-102 were simulated using various scenarios of evaporation and equilibration with atmospheric CO_2. Additionally, the metallurgical treatments undergone by the tank during its installation were simulated. The resultant simulant chemistries and thermal treatments were used in localized corrosion and stress corrosion cracking (SCC) tests. A combination of cyclic potentiodynamic polarization and potential staircase methods indicate that the secondary tank liner is not likely to suffer from localized corrosion in simulants representing the waste present in the annular space. Similarly, crack growth rate tests do not indicate an immediate threat of SCC to the secondary tank liner.

- Approaches to Probabilistic Assessment of Radioactive Waste Tank Integrity

N. Sridhar presented a conceptual Bayesian network model for estimating the probability of localized corrosion and stress corrosion cracking, considering the complexity of interconnected factors (nitrate, nitrite, pH, and temperature, etc.) leading to SCC in a tank.

5) Atmospheric corrosion

- Atmospheric Corrosion of Stainless Steels in Kuwait

The paper presented the results of a one year atmospheric exposure of four stainless steels (SSs) in Kuwait. Flat panels of SSs types UNS S31603, UNS S13895, UNS S31803 and UNS S32101 having various surface finishing conditions were exposed to the atmosphere at five sites. In addition, welded and U-bend panels of UNS S31603 were exposed to the atmosphere at the five sites. Time of wetness (TOW) and chloride deposition rates were measured. The atmospheric corrosivity of the five sites was specified according to ISO 9223 standard. Based on TOW measurements, the atmosphere corrosivity is in the range of low to medium, while based on the chloride deposition rate, the atmosphere corrosivity is in the range of low to high depending upon the closeness of the site to the sea. The panels of SSs were examined visually as well as using optical and scanning electron microscopy. The degree of corrosion attack on the SSs panels varied with the changes in micro climate, surface roughness, and the type of SS, with the welded panels showing the highest degree of corrosion attack. With regard to alloy type, the ranking accurately reflected the molybdenum content with UNS S31803 SS performing better than UNS S31603L, UNS S13895, and UNS S32101 SSs.

- Small Scale Crack Growth Sensor for Determination of AA5XXX Susceptibility to SCC

Luna Innovations Inc. presented a standalone *in situ* crack growth sensor to more accurately assess AA5XXX susceptibility to SCC. The sensor has been developed to monitor crack propagation within a surrogate tensile sample under realistic atmospheric conditions. Using tailored test specimens and exacting methods for loading, corrosive conditions and load interaction effects on SCC can be evaluated in accelerated tests and outdoor environments. These measurements can then be used to identify the significant relationships between environmental parameters and SCC failure processes. Systematically varying environmental and mechanical parameters (e.g., relative humidity, salt molarity, degree of sensitization, and stress intensity) has shown a strong dependence of crack velocity on cyclic relative humidity (RH). Specifically, an increase in crack velocity has been observed with decreasing RH.

- Effect of Relative Humidity on Corrosion of Steel under Acidified Artificial Seawater Particles

Sandia National Laboratories presented the paper. The aim of this work was to elucidate the relationship between the hygroscopic behavior of acidified artificial seawater (ASW) microparticles, as a proxy for sea salt aerosol (SSA), and the atmospheric corrosion of mild steel contaminated with them. The wetting and drying behavior of acidified ASW microparticles deposited on an inert interdigitated electrode sensor was characterized by impedance measurements. Carbon steel coupons loaded with the same contaminant were subjected to isohumidity exposures for up to 30 days. The resulting damage was quantified by optical profilometry. Sustained corrosion was detectable down to 11% RH, with significant admittance of the salt deposits on the sensor at <2% RH after 24 h, likely due to the presence of trapped electrolyte. Trends in corrosion loss versus RH were not directly reflective of the major liquid-solid phase transitions observed for particles on the sensor. The results bring into question

whether SSA-contaminated surfaces ever dry with regard to corrosion being possible in ambient outdoor environments.

- Evaluation of Atmospheric Chloride-Induced Stress Corrosion Cracking of Austenitic Stainless Steel Canister

Andy Jung from Areva presented the paper. Most canisters for spent fuel storage in the US are fabricated from austenitic stainless steel. When exposed to chloride-rich atmospheres, the welded canister is susceptible to atmospheric chloride-induced stress corrosion cracking (CISCC). CISCC may affect the confinement function as a result of crack initiation and propagation through the canister wall thickness. In this assessment, key factors affecting CISCC of the canisters are identified in terms of environments, stresses, and material sensitization. This paper proposed a methodology to estimate the time for crack initiation and crack penetration depth as a function of storage time. Furthermore, some gaps in the technical background for CISCC of stainless steel canisters are discussed.

6) Microbiologically Influenced Corrosion

- A Highly Sensitive Amperometric Sensor for Monitoring Sulfide and Microbiologically Influenced Corrosion

CanmetMATERIALS presented the paper. Microbiologically influenced corrosion (MIC) has been considered a significant factor contributing to oil and gas pipeline failures. This type of corrosion results from the activities of microorganisms in the biofilms formed on metal surfaces. The in-situ monitoring of MIC is very challenging as it requires a combination of microbiological, surface analytical and electrochemical methods. Sulfate-reducing bacteria (SRB) are considered a predominant cause of MIC and they reduce sulfate to sulfide through anaerobic respiration. Thus the microbial corrosion can be monitored through the detection of biogenic sulfide resulting from the SRB activities. In this paper, an amperometric sensor was constructed for on-line detection of sulfide. Single-walled carbon nanotubes (SWCNTs) functionalized with a conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) were used to facilitate signal transduction. The SWCNT-PEDOT-PSS modified glassy carbon electrode (GCE) sensor exhibited a large linear detection range, short response time, and high sensitivity for detection of sulfide, through direct oxidation of the sulfide without the assistance of any enzyme and mediator. The results paved the way for the development of on-line biosensors for fast and reliable monitoring of MIC related to SRB activities.

- Don’t Just Blame the SRBs and APBs for MIC

NALCO Champion presented the paper. Microbiologically influenced corrosion has historically been attributed to the activity of sulfate reducing and acid producing bacteria. Recent advances in DNA isolation and sequencing have led to the realization that these two classes of bacteria often represent only a small portion of the corrosive microbial population present in the oil and gas environment. Numerous different genera from multiple other classes of bacteria and archaea have been found to be associated with failures and are now recognized as contributors to the MIC process. The presence of these microbes, while not frequently identified through standard oil and gas industry culturing techniques, is now readily discernable through the use of Next-generation DNA sequencing platforms. This work builds on a paper from CORROSION 2014 that introduced a database with speciation results from over 4000 oilfield samples. However, the current paper discusses analyses that were performed on this database, which has grown to over 6000 samples, to discern the global distribution and relative incidence of

several classes of these newly recognized contributors to MIC; bacteria and archaea capable of iron reduction and oxidation, sulfur/sulfide oxidation, as well as methanogenesis. This new understanding of the MIC-related oilfield microbial population will allow us to design better monitoring and treatment strategies that do not simply focus on sulfate reducers and acid producers.

7) Environmentally Assisted Cracking

- Environmental Assisted Cracking of Steel Pressure Vessel in Boiler Water Service: Case Histories, Damage Mechanism Considerations, Design, and Fabrication

GE presented the paper. This paper is inspired by a series of failures that occurred in steam drums and deareators in power generation and chemical/petrochemical plants. In each case the failure occurred in non-Post Weld Heat Treated (PWHT) carbon steel (CS) and low alloy steel (LAS) welded joints and was related to the synergic action of the mechanical stresses and the chemical environment (boiler and feed water). Although technical literature has already covered and discussed the topic and the Users have experienced such damage for a long time, the primary mechanism and root causes of the failure events are still unclear. This paper shows an overview of different case histories and failure investigations related to in-service cracking of non-PWHT CS welded joints in deaerators and steam drums in some Italian power plants. The damage was associated to a sort of Environmental Assisted Cracking (EAC) related to static and/or slow rate dynamic stresses and corrosive potential of water (mainly dissolved oxygen and pH). The feedback of the failure investigations has been a starting point for a detailed design and fabrication review involving design, material selection, welding process selection, Post Weld Heat Treatments (PWHT) and Non Destructive Testing (NDT).

- Use of Double Loop-Electrochemical Potentiokinetic Reactivation (DL-EPR) to Evaluate Small Type 304 Stainless Steel Butt Welds for Susceptibility to Stress Corrosion Cracking

Bechtel Marine Propulsion Corporation presented the paper. Double Loop-Electrochemical Potentiokinetic Reactivation (DL-EPR) is a valuable technique to test Type 304 stainless steel (SS) materials and components for the presence of grain boundary chromium depletion and assess material sensitization. This has practical relevance for the evaluation of susceptibility to intergranular stress corrosion cracking (IGSCC) of welded structures. The present study reports on work to develop DL-EPR methodology applied to UNS S30400 SS pipe butt-welds of relatively small size and having fusion zones irregular in shape, both of which present experimental difficulties to electrochemical evaluations. The primary challenge was to determine how to practically get an accurate DL-EPR signal from the relatively small heat affected zone (HAZ) that may be susceptible to IGSCC. A simple method was used to isolate the area of study that led to a relatively small solution potential drops during DL-EPR measurements. Measurements on a control material showed that smaller IR drops correlated directly with a measurably smaller degree of sensitization as measured by DL-EPR. A prototypic butt-weld was used to join two different heats of materials, one of which had a low carbon with high delta-ferrite content and the other of which had a high carbon content and no delta-ferrite. The DL-EPR process could detect the delta-ferrite in the low carbon material and also isolate DL-EPR degree of sensitization measurements to the HAZ of the high carbon material. In the process of this DL-EPR analysis, comparisons were made with two different grain boundary etch techniques.

- Failure of an AISI 8630-Mod low alloy steel to C-Mn steel dissimilar metal weld, made using nickel alloy UNS N06625 welding consumables

Approximately one year after installation, it was discovered that a failure had occurred, in deep water, at a joint between an elbow from a water injection flowline and a forged connector to a subsea manifold. The line had separated at the welded joint between the AISI 8630-Mod (8630M) low alloy steel connector and the ASTM A694/A694M-031 – Grade F65 (F65) C-Mn steel elbow, made using nickel alloy UNS N06625 (Alloy 625) welding consumables. Although this type of joint is commonly employed subsea, there have been a few failures2,3 and this combination of materials is no longer preferred for this type of service.
Both halves of the fractured joint were retrieved from the seabed for failure investigation. A detailed investigation was undertaken, including extensive visual inspection, metallography and fractography, using scanning electron microscopy, to characterise the fracture event, fracture morphologies and corresponding microstructures. It was also attempted to estimate the loads which might have been responsible for fracturing the joint. In addition, supporting tests and examinations were carried out on the materials, to assess the assembly against the original construction specifications. The paper presents the observations made and discusses the failure mechanism and its relationship with the environmental conditions encountered.

- A Comparison of the C-Ring Test and the Jones Test as Standard Practice Test Methods for Studying Stress Corrosion Cracking in Ferritic Steels

Creep-strength-enhanced-ferritic (CSEF) steels have been widely implemented as water wall alloy materials in the coal-fired power industry for many years. The stress corrosion cracking (SCC) behavior of this class of materials is currently of significant interest to the industry due to recent failures. To better understand the test methods used to characterize SCC behavior in the laboratory, three representative CSEF alloys (UNS K40712, K30736, and K92460, also known in the industry as T23, T24, and T92 respectively) were subjected to two SCC test protocols: the ‘Jones Test’ set forth in DIN 50915, and the C-ring SCC test set forth in ASTM G38-01. Samples were tested in either the as-received (normalized + tempered) condition or in the normalized condition (quenched from 1065°C). Samples were exposed to aerated water in one test case and de-aerated water in a second test case for a period of 7 days at 200°C. It was found that for both test protocols, the normalized condition with aerated water led to severe cracking for all three alloys, whereas no evidence of cracking was found for the other conditions.

8) Research In Progress—Corrosion in Energy Systems

- Effect of Cold Work on Chloride-Induced Transgranular Stress Corrosion Cracking of 304L Austenitic Stainless Steel

The work was presented by Imperial College London. With the presence of residual plastic strain the crack can propagate through deformation bands without the need of contributions from the chemistry. It shows that with low cold work and dislocation density, the formation of alternative Cr rich and poor areas may speed up the crack propagation.

- Understanding the Surface Environment and Its Impact on the Extended Performance of Interim Storage Containers for Spent Nuclear Fuel

Sandia National Laboratories (SNL) presented the work. SNL is working with EPRI to collect and analyze dust samples from the curface of in-service SNF storage canisters. Samples were acquired from three different ISFSI sites- Calvert Cliffs, Hope Creek, and Diablo Canyon. It was found that in some ISFSI sites, a significant fraction of the dust was indeed chloride rich salts. However, for other sites, this was not the case. Neutron diffraction, contour method, and the deep-hole drilling method were used to characterize the stress distributions for the welds. The thermal cycling associated with the welding process altered the overall microstructure of the near-weld materials and resulted in precipitation of chromium carbides and the formation of chromium depleted regions along the grain boundaries.

- Corrosion Behavior of Copper Coated Carbon Steel for Application as Nuclear Waste Containers

Nuclear Waste Management Organization in Canada presented the paper. Electrodeposition and cold spray techniques were used to coat carbon steel with copper. Measured corrosion potentials show consistency among the electrodeposited copper, cold spray copper, and wrought copper in 3 M NaCl solution under anaerobic conditions at room temperature. No significant difference was observed before and after the anaerobic exposure to NaCl solution for 3 months. However, subtle differences were observed following galvanostatic oxidation/dissolution.

9) Research In Progress—Corrosion Modeling

- Critical Conditions for Stainless Steel Pitting Stability and Repassivation: Experiments and Modeling Using Artificial Pit Electrodes

The modeling work by University of Virginia is expected to establish an unambiguous and mathematically rigorous framework for the determination of the critical conditions characterizing stable pitting and repassivation.

- Modeling the Radiolytic Corrosion of Nuclear Fuel inside a Failed Waste Container

The work was presented by Western University, Canada. The model presented two corrosion fronts within the container if failure occurs: one on the fuel driven by the radiolysis of water by the α radiation emitted by the radiation decay process in the fuel and the other on the inside of the steel vessel leading to the dissolution of Fe^{2+} and the production of H_2. Fractures in the fuel pellets are considered. Modeling shows that the fuel corrosion rate becomes dependent on the dimensions of the fracture because the diffusive transport of H_2 into and out of the fracture determined the redox conditions.

10) Research In Progress—Passivity and Localized Corrosion

- Effects of Tantalum on the Pitting Corrosion of Super Duplex Stainless Steels

Kobe Steel. Ltd presented the work. The effect of the inclusion control by Ta addition on the pitting corrosion resistance of the duplex stainless steels was investigated. The Ta-bearing duplex stainless steel shows higher pitting corrosion resistance compared to the one without Ta addition because of MnS.

- Internal Oxidation of Ni-Fe-Cr Alloys Exposed to a Simulated Primary Water Environment

Roger Newman from University of Toronto presented the work. Ni alloys, Alloy 600 and Alloy 690, and Ni weld metals, Alloy 82 and Alloy 52, were exposed to a 480 °C hydrogenated steam environment, considered to simulate primary water in nuclear plants. The external and/or internal oxidation behavior of the different alloys was studied. Oxygen was found to penetrate both intra- and intergranularly in Alloy 600 resulting in the expulsion of metallic Ni to the surface. Internal oxidation was observed intragranulaly in Alloy 690 due to hindered lattice kinetics not allowing for sufficient Cr diffusion to the surface, even with the high Cr content; external surface oxidation was observed at grain boundaries which act as a short circuit for fast Cr diffusion. Dilution from parent materials led to a heterogeneous composition across Ni alloy weld metals resulting in different oxidation tendency from root to crown.