CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

TRIP REPORT

SUBJECT: NACE 2004 Corrosion Conference & Exposition
Project Number 20.06002.01.081; AI Number 06002.01.081.322

DATE/PLACE: March 28–April 2, 2004
New Orleans, Louisiana

AUTHORS: G.A. Cragnolino, D.S. Dunn, and L. Yang

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PERSONS PRESENT: G.A. Cragnolino, D.S. Dunn, and L. Yang (CNWRA), and about 5,500 representatives from various countries and organizations.

BACKGROUND AND PURPOSE OF TRIP:

The annual NACE 2004 Corrosion Conference & Exposition features technical symposia, technical committee meetings, and an exhibitor show. The main goals of attending the conference were to:

- Present papers authored by the CNWRA staff that were included in a several symposia
- Attend presentations from the DOE high-level waste program and work supported by the State of Nevada
- Make contacts with prospective candidates to fill open positions within the CNWRA
- Keep abreast of technical advancements in the corrosion science and engineering

In addition to presentations in the technical symposia, CNWRA staff played an active role in the organization of the several symposia and participation in technical committee meetings.

SUMMARY OF PERTINENT POINTS:

Papers co-authored by the CNWRA staff and presented at the NACE 2004 Corrosion Conference are listed below:

"Effect of Fabrication Processes on Alloy 22 Corrosion Resistance," D.S. Dunn, G.A. Cragnolino, Y.M. Pan, and L. Yang.

"Studies of the Corrosion Behavior of Stainless Steels in Chloride Solutions in the Presence of Sulfate Reducing Bacteria," L. Yang and G.A. Cragnolino.

Papers presented were well received and prompted questions and subsequent discussion.

Corrosion in Nuclear Systems

The Corrosion in Nuclear Systems contained 12 papers focused on corrosion in reactors and 16 papers on corrosion in waste storage or disposal systems.

Most of the papers focused on corrosion in reactor systems dealt with the recurrent problem of stress corrosion cracking in pressurized water reactors and boiling water reactors covering stainless steels such Type 304 and 316NG and nickel base alloys such as Alloys 600 and 690.

There was a paper by Farina and Duffo (CNEA, Argentina) presented by R. Rebak on the stress intensity conditions required for the transition from intergranular to the fast transgranular cracking in zircaloy exposed to iodine dissolved in various alcohols. It was claimed that the transition occurs at low stress intensities {$K_I = 11$ MPa·m$^{1/2}$ [10 ksi·in$^{1/2}$]}, regardless of the hydrocarbon chain of the alcohol, and also at the same K_I value that in aqueous chloride solutions.

Bo Rosborg (Rosborg Consulting, Sweden) presented a paper entitled real-time monitoring of copper corrosion at the Äspö hard rock Laboratory. The Äspö Hard Rock Laboratory, completed in 1995 was a test site for the siting and construction of the future deep repository for spent nuclear fuel in Sweden. Specimens made of copper, a container candidate materials for Swedish high level waste disposal program, had been placed in bentonite blocks in the test sites. These coupon tests was and will be run for 1, 5 and 20 years. Along with the coupon tests, preliminary real-time corrosion monitoring was conducted with cylindrical copper electrodes in the test sites since May 2001 using a SmartCET system manufactured by InterCorr International (Houston, Texas). The system operates in a multi-technique mode. The polarization resistance and harmonic distortion analysis technique were used to measure the general corrosion rate and the electrochemical noise technique was used to detect localized corrosion. The measured corrosion rate of the copper electrodes was 0.5 μm/y [0.02 mpy]. This value is considerably lower than the average corrosion rate of about 3 μm/y [0.12 mpy] estimated from retrieved copper coupons. The recorded localized corrosion signal (from the electrochemical technique) appeared to indicate pitting corrosion. However, examination of already retrieved copper coupons has not revealed any obvious signs of pitting.

F. Hua (Betchel SAIC Company) presented a comprehensive review of the information available on the open literature on uniform corrosion, localized corrosion, stress corrosion cracking, and hydrogen embrittlement of Ti alloys. The paper also included microbially influenced corrosion, radiation-induced corrosion, and the effects of fluoride and bromide. It was concluded that Ti-Grades 7 and 24 will not be degraded during the 10,000-year regulatory performance period by the corrosion processes listed above. Nevertheless, some of the conclusions (e.g., the threshold hydrogen for hydrogen induced cracking of Ti-Grade 24) seems to be reached without a solid experimental backup but based on analogies with similar alloys.

The performance assessment model for localized corrosion susceptibility of Alloy 22 in potential Yucca Mountain repository was presented by J.H. Lee from Sandia National Laboratory (SNL). The localized corrosion susceptibility of Alloy 22 was determined using data acquired at LLNL and other project data. Localized corrosion susceptibility is determined by comparing the corrosion potential to the repassivation potential for localized corrosion. The repassivation potential was found to be a function of chloride concentration, nitrate concentration, the nitrate to chloride concentration ratio and temperature. The corrosion potential was determined to be a function of pH, chloride, concentration, temperature, and the nitrate to chloride concentration ratio. The work presented was a summary of the localized corrosion model described in the Localized Corrosion of the Waste Package Outer Barrier Analysis and Model Report.

An assessment of the damage to Alloy 22 by pitting corrosion in simulated disposal environments was presented by D.D. Macdonald from PSU. Damage functions describing distribution of pit sizes were obtained by anodic polarization of Alloy 22 in saturated sodium chloride solutions for times up to 180 days. The applied potentials were very high and grain boundary etching typical of transpassive dissolution was observed. The assessment of corrosion damage considered damage from pits and did not include attack at grain boundaries. Neglecting processes that may result in repassivation of localized corrosion, the deepest pits would penetrate the waste package outer barrier within 10,000 years. Considering repassivation processes decreases the maximum pit depth, the penetration of the waste package outer container is not predicted.

Results of corrosion tests conducted at Catholic University for the State of Nevada were presented by A. Pulvirenti. The corrosion tests were conducted by placing foils of Alloy 22 in flasks with simulated concentrated unsaturated zone pore water (62x and 1243x concentrated pore water). After the majority of the water had evaporated, a condenser was placed on the flask to prevent evaporation of the remaining solution. Decomposition of the magnesium nitrate and magnesium chloride resulted in the formation of both hydrochloric and nitric acid. The acid gasses were condensed resulting in a solution pH less than 1 and a boiling point in excess of 120 °C [248 °F]. Rapid corrosion rates for Alloy 22 {up to 1 mm/year [39 mpy]} were noted in this solution.

Stress corrosion crack propagation rates for Alloy 22 and Ti-Grade 7 were reported by P. Andresen (General Electric Global Research Center). The paper was an update to work presented previously. For alloy 22, cracks could be initiated using low frequency cyclic loading. When the cracks were transitioned from cyclic loading to a constant stress intensity, the crack propagation rates decreased to values below 4×10^{-10} mm/second [1.5×10^{-11} in/second] and arrest of crack growth was observed in several cases. Higher crack propagation rates were observed for cold worked or welded Alloy 22. Crack propagation rates for Ti-Grade 7 were in the range of 3×10^{-10} to 1×10^{-8} mm/second [1.2×10^{-11} to 4×10^{-10} in/second] and crack arrest was not usually observed after the specimens were transitioned from cyclic loading to constant stress intensity.

The effects of environment and alloy composition on the electrochemical behavior of nickel-chromium-molybdenum alloys was presented by J. Hayes from LLNL. The corrosion resistance and passive film composition was examined on Alloy 22 Ni-11Cr-7Mo, and Ni-20Cr. The passivity and composition of the oxide film of these three nickel alloys are a strong function of the solubility of the metal oxides. The behavior of mill-annealed and welded Alloy 22 were undistinguishable when polarized anodically in 1 M NaCl solution of pH 2.8, 7.5 and 11 at 90 °C [194 °F].

General corrosion rates for Alloy 22 in simulated Yucca Mountain groundwater solutions was presented by J.H. Lee from SNL. The performance assessment abstraction, which uses the measured corrosion rate of samples exposed for periods up to 5 years in the long-term corrosion test facility at LLNL, is described in the Localized Corrosion of the Waste Package Outer Barrier Analysis and Model Report. The uniform corrosion rate was observed to decreases from initial values of 1 μm/year [0.04 mpy] after exposures for 1 year to approximately 0.01 μm/year [4×10^{-4} mpy] after 5-year exposures. A subsequent paper presented by L. Wong from LLNL, details of the results of the long term corrosion test samples were presented. In simulated concentrated water, calcium carbonate deposits were observed on the specimens. Iron rich reposits were observed on specimens tested in simulated acidified water. The iron deposits may have come from stainless steel specimens in exposed in the same tanks or from a steel labeling tool used to stamp the specimens. The average corrosion rate of the specimens was less than 15 nm/year [6×10^{-4} mpy] and the maximum corrosion rate was 2 nm/year [8×10^{-5} mpy]. The higher corrosion rates for the crevice specimens may be caused by several factors including a coarse surface finish. The crevice specimens may have also been produced with a mill finished surface. While the analyses of the test specimens used at LLNL did not indicate chromium and molybdenum depletion in the near surface layers, previous work has shown that the mill finished surface layer can have a faster corrosion rate as a result of alloy depletion. This may account for the higher corrosion rates for the crevice specimens which were free from crevice corrosion.

Environmentally Assisted Cracking

The Environmentally Assisted Cracking Symposium featured 26 papers including papers form Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL). Results of slow strain rate testing of Alloy 22 in simulated concentrated water were presented by K.J. King from LLNL. Stress corrosion cracking, which was observed at temperatures as low as 65 °C [149 °F], increased with temperature and potential. No stress corrosion cracking was observed in either 1 M or 4 M NaCl. Some incipient cracks were observed in 1 M NaF at anodic potentials. Hydrogen induced cracking was observed at ambient temperatures at very low cathodic potentials whereas no cracking was observed at elevated temperatures. The results of U-bend tests conducted in the long-term corrosion test facility (LTCTF) at LLNL were presented by R. Rebak. No stress corrosion cracking was observed on any of the U-bend specimens tested in simulated acidified water, simulated concentrated water, and simulated dilute water after 5 years exposure.

R. Rebak (LLNL) also presented the results of tests conducted at the LTCTF using welded and non-welded U-bends of various Ti alloys exposed to both the liquid and vapor phase in simulated acidified water, simulated concentrated water, and simulated dilute water at two temperatures {60 and 90 °C [140 and 194 °F]}. Ti-Grade 12 and Ti-Grade 16 were tested for 5 years whereas Ti-Grade 7 was tested for 2.5 years. Rebak reported that from 184 specimens tested, only three welded specimens of Ti-Grade 12 exhibited stress corrosion cracks in the liquid phase of simulated concentrated water at 90 °C [194 °F].

Stress corrosion cracking of 316L stainless steel used for storage of plutonium-containing salts was presented by R.S. Lilliard from LANL. Crack growth measurements were conducted with compact tension specimens. Pitting corrosion was observed on the interior surfaces of the containers as a result of the deliquescence of chloride containing salts that may serve as initiation points for stress corrosion cracking.

Process Industry Corrosion

The Process Industry Corrosion in the New Millennium Symposium contained papers on alloy selection, welding processes, and environmental effects that are of interest to the chemical process industry. A comparison of Alloy 22 and Alloy 59 filler metals for nickel-chromium-molybdenum alloys was presented by J. Heinemann from UTP Schweissmaterial GmbH. Tests were conducted using standard oxidizing acid chloride test solutions. Base metals, including Alloys C-276, C-22 and 59, were welded using gas tungsten arc welding and shielded metal arc welding. Lower corrosion rates of base metals welded using Alloy 59 were attributed to the lower iron and higher chromium contents of Alloy 59. In a subsequent paper, the effect of shielding gas composition on the weldability of nickel-chromium-molybdenum alloys using pulsed gas metal arc welding was presented. Small additions of CO_2 (0.05 percent) were used for arc stabilization. Additions of He (30 percent) used to promote heat transfer and improve wetting, and small amounts of H_2 (2 percent) were added to increase travel speed, and constrain the arc. Compared to pure Ar, the mixed gas reduced splatter, increased travel speed and reduced the irregular fusion line. The addition of small amounts of CO_2, for arc stabilization, did not result in increased carbon contents in the welds. Using standard acidic oxidizing chloride accelerated tests, similar corrosion rates and critical pitting temperatures were observed with Alloy 22 welds using the mixed shielding gas and pure Ar shielding gas.

Corrosion in Super Critical Water Systems

This was a very interesting symposium organized and chaired by R. Latanision (a member of the Nuclear Waste Technical Review Board). The interest in supercritical water systems arises from their application on the oxidative degradation of chemicals used in weapons of mass destruction and more recently on their possible application to a new generation of nuclear power plants following the successful experience with fossil fired power plants. As in other applications corrosion is a great concern and in particular stress corrosion cracking. D.D. Macdonald [Pennsylvania State University (PSU)] presented an overview on the relevant issues related to the understanding of corrosion and electrochemical processes in supercritical aqueous media, in which the need of appropriate reference and pH electrodes was emphasized. His presentation was followed by 9 papers covering materials degradation, experimental measurements and techniques and specific studies on oxidation of chlorinated substances.

G. Was (University of Michigan) had very comprehensive presentation on corrosion and stress corrosion cracking of iron-and nickel-base austenitic alloys. Type 304 L stainless steel and Alloy 625 were found to be susceptible to intergranular stress corrosion cracking using slow strain rate tests in deaerated supercritical water at 500 °C [932 °F] whereas 316L and a Alloy 690 only experienced ductile failure exhibiting minor cracks on the tensile specimen side surface. The compositional profiles of the oxide films formed on the surface were characterized in depth in cross sectional specimens using a scanning electron microscope combined with energy dispersive spectroscopy.

Y. Watanabe (Tohoku University) showed that stress corrosion cracking occurred on stainless steels in supercritical water of very low dielectric constant (approximately 2.5) which is like a dense gas without the properties of a ionic conducting medium suggesting that anodic dissolution is not involved in the crack advance mechanism.

Online Sensors for Localized Corrosion

L. Yang chaired a workshop on Online Sensors for Localized Corrosion during the TEG 100X committee meeting. This workshop was well participated by the experts on corrosion monitoring. There were seven presentations. Three of them were on field applications of coupled multielectrode array sensors, two of them were on the laboratory studies of corrosion using coupled multielectrode sensors, two of them were on electrochemical noise method and its applications both in the laboratory and in the fields. The results from the coupled multielectrode array sensors appeared to suggest that it is a good candidate as a tool for performance confirmation.

Technical Committee Activities

D. Dunn (CNWRA) participated in the Technical Committee Meeting on Environmentally Assisted Cracking and was selected as vice-chair for the next Technical Symposium on the subject to be held during CORROSION 2005 Conference in Houston, Texas. G. Cragnolino (CNWRA) attended the Technical Committee Meeting on Corrosion in Nuclear Systems. In addition to the business of the committee, G. Ilevbare (LLNL) made a presentation on electrochemical studies of Alloy 22 conducted as a part of the Yucca Mountain program. Cragnolino also participated as a member in the Research Committee Meeting and was selected vice chair for the next Topical Research Symposium on Corrosion Resistant Alloys for Extreme Environments. L. Yang (CNWRA) attended the Specific Technology Group Meeting on Science and Engineering Applications and Methods of Corrosion Monitoring and Measurements (STG 62) and proposed to form a new Technology Exchange Group (TEG) on Laboratory and Field Applications of Multielectrode Sensors. His proposal was approved by the STG steering committee and submitted to the NACE International Program Coordinators for final approval. If approved, L. Yang will be the chair of this new TEG and a Technical Symposium on Multielectrode Corrosion Sensors will be organized for CORROSION 2006 Conference.
L. Yang was selected to be the chair for the next Technical Symposium of the Corrosion and Corrosiveness Sensor Development Technology Exchange Group (TEG 100X) on Corrosion Sensors for On-line Monitoring to be held during CORROSION 2005 Conference in Houston, Texas.

SUMMARY OF ACTIVITIES:

None.

CONCLUSIONS:

The conference provided an opportunity to follow the activities related to the potential repository at Yucca Mountain supported by the DOE and the State of Nevada. In addition, many symposia had papers that are relevant to the performance of engineering alloys that are used in reactors as well as those that may be used in the potential repository.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

None.

RECOMMENDATIONS:

Attendance at future NACE CORROSION conference is highly recommended as well as participation in selected committee meetings.

SIGNATURES:

Darrell S. Dunn — 4/9/2004
Principal Engineer — Date

Gustavo Cragnolino — 4/9/2004
Institute Scientist — Date

Lietai Yang — 4/9/2004
Senior Research Engineer — Date

CONCURRENCE:

4/9/04

Vijay Jain, Manager
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04/09/2004

Budhi Sagar
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Date

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