CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES TRIP REPORT

SUBJECT: 204th Meeting of The Electrochemical Society 06002.01.071.008

- DATE/PLACE: October 12–16, 2003 Orlando, Florida
- AUTHOR: L. Yang

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PERSON(S) PRESENT:

The meeting was attended by scientists, researchers, students from various universities, government and private research organizations in the United States, and other countries including Japan, Korea, United Kingdom, Germany, France, and Sweden. L. Yang from the Center for Nuclear Waste Regulatory Analyses (CNWRA) participated in this meeting.

BACKGROUND AND PURPOSE OF TRIP:

The Electrochemical Society Meeting is held twice a year, once in the spring and again in the fall. The 204th meeting was held October 12–16, 2003, at the Wyndham Palace Hotel, Orlando, Florida. The purpose of staff attending this meeting was to present a paper in the atmospheric corrosion session and to keep up-to-date with recent developments in various theories and methods in the studies of corrosion, especially humid air corrosion, and model predictions of metallic components. The corrosion of carbon steel support structures, drip shields and waste package containers is one of the main processes that would cause the deteriation of the engineered barrier system in the potential repository at Yucca Mountain, Nevada. Depositions of aerosol and dust from ventilation air and the evaporation of groundwater may lead to the accumulation of hygroscopic salts on the surfaces of these metal components. At relative humidities at or above the deliquescence relative humidity of the hygroscopic salts, moisture in the air may be absorbed by these salts and form highly concentrated solutions and cause corrosion of the metal components under the atmospheric conditions.

SUMMARY OF PERTINENT POINTS:

The meeting was organized into 36 sessions and symposia, including a total of 1,451 oral presentations and posters, covering a wide range of topics such as corrosion, batteries and energy, electronics, and electrolysis. The sessions and symposia most pertinent to nuclear waste management program included: (i) atmospheric corrosion mechanisms; (ii) corrosion and protection of light metal alloys; (iii) surface oxide films; (iv) biological nanostructures, materials, and applications. The summary provided in this report includes a CNWRA staff presentation; the U.S. Department of Energy (DOE) and its contractors' work in the areas of corrosion and life prediction of engineered metallic structures; and presentations from other organizations on corrosion.

L. Yang (CNWRA) made a presentation on The Study of Atmospheric Corrosion of Carbon Steel under Salt Deposit Using Coupled Multielectrode Array Sensors. In this work, coupled multielectrode array sensors that were recently developed at CNWRA were used to measure the nonuniform corrosion of carbon steel under a potassium chloride salt deposit in a humidity controlled environmental chamber. The sensing electrodes in a multielectrode array are coupled to simulate one piece of metal, and the currents that flow from the anodes (or more anodic electrodes) to the cathodes (or less anodic electrodes) are measured as the corrosion signal. The experiments were conducted at 49 °C [120 °F]. Prior to the test, both the salt powder and the sensors were dried separately at a low relative humidity. After the drying step. the salt was placed on top of the sensors inside the humidity chamber. The relative humidity in the chamber was rapidly lowered to 35 percent. After being held at about 35 percent, the relative humidity in the chamber was slowly increased to the deliquescence relative humidity of the potassium chloride. The relative humidity of the chamber was held at or above the deliguescence relative humidity to allow corrosion to occur for a predetermined time. Then, the relative humidity was decreased slowly to determine the relative humidity at which the corrosion process on the sensor surface would stop. The measurement showed that the nonuniform corrosion current from the sensors started to increase at approximately 67.4 percent relative humidity, which is about 14 percent lower than the deliguescence relative humidity for potassium chloride (81.3 percent). The measurement also showed that once nonuniform corrosion has occurred on the sensor, corrosion continued even at a relative humidity of 27 percent. The lowering of the relative humidity at which corrosion takes place was attributed to the formation of corrosion products within the corroded pits or crevices.

G. llevbare (Lawrence Livermore National Laboratory) presented a paper entitled The Effect of Welding on the Crevice Breakdown and Repassivation Potentials of Alloy 22 in 5 M CaCl₂ between 45 °C [113 °F] and 120 °C [248 °F]. In this paper, critical breakdown potentials, E_{crit} , repassivation potentials, E_{p} , and corrosion potentials were measured as a function of temperature on wrought and welded creviced Alloy 22 samples in 5 M CaCl₂ between 45 °C [113 °F] and 120 °C [248 °F]. It was reported that the E_{crit} , and E_{p} were similar for both the wrought and the welded samples at the temperatures tested. The reported E_{p} values were from 0 to -180 mV_{SEC} when temperature changed from 60°C [140 °F] to 90 °C [194 °F] and 120 °C [248 °F]. The reported corrosion potentials decreased slightly from -280 mV_{SCE} to -350 mV_{SCE} when the temperature changed from 45 °C [113 °F] to 120 °C [248 °F]. However, in response to questions, the author stated that the corrosion potential was measured when the system was purged with high purity nitrogen. Transpassive dissolution was considered as the dominant mode of oxide film breakdown on Alloy 22 at 45 °C [113 °F] and 60 °C [140 °F] on the base metal, and at 60 °C [140 °F] on the welded specimens.

T. Lian, M. Whalen, and J. Estill from Lawrence Livermore National Laboratory were scheduled to present a paper entitled Environmental Influences on Corrosion Behavior of Titanium Grade 7. However, the presentation was canceled because the presenter failed to show up. According to the symposium abstract, this paper was intended to summarize the recent work conducted at the Lawrence Livermore National Laboratory in evaluating the corrosion behavior of Titanium-7 under a variety of testing environments. The authors conducted polarization experiments in fluoride-containing 4 M NaCl solutions and the preliminary results showed that a significant increase in passive dissolution rate of Titanium-7 was found when fluoride concentration was increased from 0.01 M to 0.1 M. They observed a strong effect of temperature and chloride concentration on corrosion rate with the presence of fluoride. At the time the abstract was

prepared, the authors planned to use electrochemical impedance spectroscopy in conjunction with a potentiostatic scan to study the transformation in corrosion behavior as a function of palladium enrichment on metal surface. The authors also planned to use several analytical techniques including x-ray photoelectron spectroscopy, Auger electron spectroscopy, and scanning electron microscopy to characterize the surface properties.

M. Urquidi-Macdonald from Pennsylvania State University presented a paper, Prediction of Transient Passive Film Growth on Alloy C-22. The work was sponsored by the DOE Yucca Mountain Project through Innovative Design Technologies. In this paper, point defect model was used to analyze the rate of change in thickness of the barrier layer of the passive film on Alloy 22. According the point defect model, the transients in film thickness and current for Alloy C-22 were calculated upon stepping the applied voltage over the cycle 0.5 V_{SCE} -> 0.6 V_{SCE} -> 0.3 V_{SCE} -> 0.0 V_{SHE} -> 0.3 V_{SHE} -> 0.6 V_{SHE} in a solution of pH = 6 at 25 °C [77 °F] and 90 °C [194 °F]. The transients were used to determine the conditions under which the corrosion of Alloy 22 containers may be predicted using quasi steady state models. It was reported that the authors were able to identify the processes that lead to film growth and thinning in response to positive and negative potential steps, respectively. Using a neural network model, the authors were able to obtain the model results that agree well with the experimental data on oxide growth.

D. Macdonald (Pennsylvania State University) presented a paper, the Role of Chloride Ion in Passivity Breakdown on Nickel. In this paper, the authors assessed the impact that chloride has on the electronic and point defect structures of the passive state on nickel. The author showed that, as the concentration of Cl⁻ in pH 8.5 borate buffer solution increases, the concentration of metal vacancies in the passive film on nickel metal also increases. The addition of Cl⁻ to pH 8.5 borate buffer solution after passivity had been established in the absence of Cl⁻ also resulted in an increase in the concentration of metal vacancies in the passive film. Using electrochemical impedance spectroscopy, they showed that the observed increase in cation vacancy concentration in the passive film was due to chloride-catalyzed ejection of cations from the film/solution interface. The authors believed that this finding supports the point defect model, but is inconsistent with the chloride-catalyzed film dissolution and chloride penetration mechanisms for passivity breakdown.

D. Macdonald also presented another paper, Theory for the Deterministic Prediction of Pitting Corrosion Damage on Aluminum. This paper reviewed the theoretical basis of damage function analysis and the deterministic prediction of damage due to pitting corrosion. Damage function analysis was applied to the case of the pitting corrosion of aluminum in chloride-containing solutions. Expressions were given for the differential damage function and the integrated damage function, in terms of models for the progressive nucleation, growth, and repassivation of individual pits. The authors stressed the usefulness of damage function analysis in predicting the accumulation of pitting corrosion damage on pure aluminum over wide ranges of chloride activity and the rate of delayed repassivation for stable pits. The author concluded that damage function analysis is a powerful and practical tool for predicting the accumulation of corrosion damage in a wide variety of systems under conditions that are difficult to measure experimentally because the component models are calibrated under one set of conditions and then accurately predict localized corrosion damage accumulating under other sets of conditions.

C. Davis (University of Calgary, Canada) presented a poster on Electrochemical Characterization of Biofilm Growth on Platinum Surfaces. In this presentation, the authors attempted to use an electrochemical method to detect microbial adhesion. The goal was to establish the stages of biofilm development such that bacterial attachment would be identified long before pitting could occur. The open circuit potential, electrochemical impedance, and cyclic voltammetry methods were investigated as means of biofilm detection. It appears that the authors were able to derive significant signals corresponding to the biofilm growth. As only platinum electrodes are used, the sensors may be made robust for conditions found under the proposed repository conditions and therefore may be used for the performance confirmation if the development of sensors is successful.

IMPRESSIONS/CONCLUSIONS

The sessions and symposia that are relevant to corrosion were well attended. A significant number of papers were presented in the area of model development for life predictions of metallic components. The development of mechanistic models for the long term behavior of the proposed waste package container, Alloy 22, may help increase the confidence of the empirical models that are based on relatively short-term experimental results.

PROBLEMS ENCOUNTERED:

None.

PENDING ACTIONS:

None

RECOMMENDATIONS:

Attendance at future Electrochemical Society Meetings with sessions or symposia that are relevant to corrosion is recommended to keep up-to-date with advances in corrosion studies. The meeting provides a good forum to learn technical information, and allows gathering of feedback from the peer community on the technical work performed at the CNWRA.

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