August 4, 2003

MEMORANDUM TO: Martin Virgilio, Director
Office of Nuclear Material Safety
and Safeguards

THROUGH: John Greeves, Director **/RA/**
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

FROM: Tae M. Ahn **/RA/**
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SUBJECT: TRIP REPORT ON DISCUSSION WITH WORLD RENOWNED EXPERTS ON THE ALTERNATIVE CORROSION MODELS; MANCHESTER, U.K., AND TSUKUBA CITY AND OSAKA, JAPAN, JUNE 25 TO JULY 4, 2003

Attached is a trip report documenting the consultation of Tae M. Ahn of the Division of Waste Management (DWM) with world renowned experts on the alternative corrosion models to assess the waste package container lifetime in the disposal of high-level waste. The meetings were held with professor R. Newman of the University of Manchester Institute of Science and Technology, Manchester, U.K., and Dr. T. Shinohara of National Institute for Materials Science, Tsukuba City and professor S. Fujimoto of Osaka University, Osaka, Japan. Highlights of the trip are provided as Attachment 1 to this memorandum. This report expands upon a "quick look" report prepared on July 14, 2003. DWM believes the content of this report is likely to be of limited interest to the Commission.

Attachment: As stated

cc: W. Dean (OEDO)
J. D. Lee (OIP)
T. Rothschild (OGC)
L. Silvious (ONSIR/INFOSEC)
M. Federline (NMSS)
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NRC FOREIGN TRIP REPORT

Subject
Discussion with world renowned experts on the alternative corrosion models to assess the waste package (WP) container lifetime in the disposal of high-level waste (HLW)

Dates of Travel and Countries/Organizations Visited
June 25 to July 4, 2003; The University of Manchester Institute of Science and Technology (UMIST), Manchester, U.K., National Institute for Materials Science (NIMS), Tsukuba City, Japan, and Osaka University (U.), Osaka, Japan

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Sensitivity
Non-Sensitive

Background/Purpose

Currently, the Department of Energy's (DOE) safety case of the proposed Yucca Mountain (YM) repository relies heavily on the robust container. The long-term container life is in turn determined by its resistance to aqueous corrosion. However, the history of the corrosion performance of engineering alloys is very short (a few decades), compared with the long compliance time, 10,000 years. Nonetheless, The Code of Federal Regulations Section 10 Part 63 requires the sound technical basis for the corrosion models used in the DOE's Total System Performance Assessment (TSPA). Experimentation, modeling and analogue inference have been the basis for the mechanistic understanding that will build confidence in the long-term prediction of the repository system. Currently the best corrosion models for various corrosion processes are selected and used in the DOE's TSPA Code. These include uniform dissolution and the integrity of passive film, the critical potential for localized corrosion, and the threshold stress intensity for stress corrosion cracking (SCC). As in the nature of modern science, there are also potentially risk significant alternative models for these corrosion modes. The Code of Federal Regulations Section 10 Part 63 requires DOE to evaluate alternative models.

There are a number of renowned scientists working on each of the various corrosion modes. R. Newman of UMIST, U.K., is the lead in developing the theories of passivity and of passivity breakdown leading to localized corrosion/SCC. T. Shinohara of NIMS and S. Fujimoto of Osaka U., both in Japan, have established extensively related theoretical bases. The staff consulted with them on the alternative corrosion models to assess the WP container lifetime in the HLW disposal and subsequently to develop the alternative models with the NRC Total-system Performance Assessment (TPA) Code. During the visit, the staff presented a summary of work done at the NRC related to modeling of uniform corrosion, localized corrosion, and SCC.

Abstract: Summary of Pertinent Points/Issues

The staff consulted with world renowned experts on corrosion models to assess the WP container lifetime in the HLW disposal. The meetings were technical in nature which provides an opportunity for the NRC staff to obtain expert views on corrosion models that are used in the reviews of the DOE's License Application of a HLW geologic repository at the YM site. No sensitive information was discussed during these meetings nor any policy decisions affecting NRC were discussed. The interaction was very intensive and the desired information exchange was fully achieved.

Discussion

The staff focused his discussion on (1) the critical potential for localized corrosion and (2) issues involved in uniform corrosion and SCC. For Alloy 22 WP material in the proposed YM repository, the localized corrosion is considered more risk significant compared with uniform corrosion and SCC. Data on uniform corrosion from various tests, models and analogs suggest a WP lifetime exceeding 10,000 years. It appears unlikely that SCC would occur. Furthermore, SCC can be also mitigated by applying compressive stress. However, currently both DOE and NRC have concerns that localized corrosion could occur above approximately 90° C depending on the various deliquescence salts deposited on the WP surface. The DOE and NRC's current assessment of the localized corrosion is based on generally accepted conservative critical potentials for localized corrosion. Unlike SCC, localized corrosion may not be easily mitigated by design, and WP perforations from the localized corrosion may grow continuously.

(1) the critical potential for localized corrosion:

Because the currently adopted repassivation potential as the critical potential is considered too conservative by DOE and the corrosion community, it is important to evaluate alternative models. The group formerly led by T. Shinohara originally proposed the use of the repassivation potential for industrial applications. R. Newman and S. Fujimoto group further established independently theoretical bases. DOE and NRC have developed rationales for its use in the long-term repository.

During this trip, the staff and the three groups (UMIST, NIMS and Osaka U.) examined various interpretations of the critical potentials including the repassivation potential in more popular systems such as stainless steels for industrial applications. Many uncertainties in the theoretical model for localized corrosion were identified and discussed. Examples include (a) relationships among critical potentials, depassivation pH and critical chemistry, (b) shift in potential for crevice corrosion either in anodic direction or in transpassive direction, and (c) relationship between initiation potential and repassivation potential.

Based on this discussion, these three groups acknowledged and commented on the current DOE and NRC's efforts to achieve more realistic and less conservative criteria that take into consideration the effects of alloying elements such as molybdenum and of inhibitors such as nitrates. In addition, they informed the temperature regime of low repassivation potentials. Ni-Cr alloys in sulphate containing high-temperature high-pressure water solutions (Osaka U.) and Ti-based alloys in chloride solutions (NIMS) showed that the repassivation potentials increase above around 100° to 150° C. These groups also questioned applicability of critical potential models to predict long-term behavior. The current laboratory electrochemical measurements may not be stable in the repository time scale. Accumulated corrosion products may alter the aqueous chemistry adjacent to bare metal by the selective aqueous species transport through the corrosion products (UMIST). NIMS observed this phenomenon in their atmospheric corrosion tests of steels. The corrosion products can also act as some large surface cathodes to accelerate uniform corrosion (NIMS).

(2) issues involved in uniform corrosion and SCC:

- Stress redistribution after SCC propagation may not be significant in arresting continuous crack growth, according to the UMIST research.
- Anodic sulphur segregation in Alloy 22 potentially leads to accelerated uniform corrosion. This may be interpreted similarly to tungsten or other metal segregation in aluminum alloys. UMIST has extensive research experience in aluminum alloys.
- Density and size of pits may remain constant for a long period of time with the separation of cathodes or pit penetration through the wall. However, this needs confirmation.
- Although a lead-induced SCC is unlikely, R. Newman cautioned that at grain boundaries of oxides, lead may be accumulated and could be mobile to expose bare metal to accelerated corrosion.
- Ti alloys may have an optimum cathodic condition under which Ti^{2+} is stable and hydrogen absorption is maximized (Osaka U.).
- There were different views on the effects of sulphate ions as an inhibitor. Whereas UMIST and NIMS agree with the inhibiting roles to localized corrosion, Osaka U. observed that sulphate ions promoted the passivity breakdown of Ni-Cr alloys in high-temperature high-pressure water.
- Osaka U. does not believe that DOE's seemingly anodic peak of Alloy 22 in simulated dilute and simulated concentrated YM groundwaters would disappear in long-term period. They often observed these peaks in Ni-Cr alloys in high-temperature high-pressure water.
- The groups discussed other topics relevant to repository corrosion issues. These include thin film aqueous corrosion (NIMS), photochemical study of passive film (Osaka U.), surface modifications for corrosion protection by laser (UMIST) and by the coating semiconducting titanium dioxide (NIMS), extreme pit size analysis (UMIST), and hydrogen embrittlement of Ni-based alloys (Osaka U.).

Pending Actions/Planned next Steps for NRC:

The outcomes of the discussion will be incorporated (1) in the future NRC and the Center for Nuclear Waste Regulatory Analyses (CNWRA) Operations Plan for FY04 and (2) in the future NRC/DOE technical exchanges and Appendix 7 meetings. This type of interaction offered an excellent short-term rotational experience by working intimately with world renowned experts. The staff highly recommend that staff seek similar opportunities to participate in this type of interaction with various experts.

Points for Commission Consideration/Items of Interest

No Commission action is required as a result of this trip.

Attachment

(A) List of Pertinent Documents
(B) A Copy of Business Cards Collected

"On the margin"

None

Attachment (A). List of Pertinent Documents

(1) M. I. Abdulsalam, T, Shinohara, H. Suzuki, and T. Shigeo, Effect of Electrode on Solution Chemistry Inside a Crevice, Proc. 48th Japan Corrosion Conference on Materials and Environments, 2002 (under translation)

(2) N. J. Laycock and R. C. Newman, Localised Dissolution Kinetics, Salt Films and Pitting Potentials, Corrosion Science, p. 1771, 1997

(3) N. J. Laycock, R. C. Newman, and J. Stewart, Comparison of Passive - Dissolution and Micro - Pitting Models for the initiation of Crevice Corrosion in Stainless Steel, Proc. of International Symposium on Plant Aging and Life Predictions of Corrodible Structures, 1995

(4) P. Ernst and R. C. Newman, Pit Growth Studies in Stainless Steel Foils. I. Introduction and Pit Growth Kinetics and II. Effect of Temperature, Chloride Concentration and Sulphate Addition, Corrosion Science, p. 927, 2002

(5) T. Shibata and S. Fujimoto, Breakdown of Passive Film on Ni-Cr Alloys in High-temperature High-Pressure Water Containing Sulfate Ions, T. Shibata and S. Fujimoto, Corrosion, p. 793, 1990

(6) T. Shibata and S. Fujimoto, Straining Electrode Behavior of Fe-Cr and Ni-Cr Alloys in High Temperature and High Pressure Borate Buffer Solution, Transac. of the Japan Institute of Metals, p. 424, 1987

(7) H. Habazaki, K. Shimizu, P. Skeldon, G. E. Thompson, G. C. Wood and X. Zhou, Nanoscale Enrichments of Substrate Elements in the Growth of Thin Oxide Films, Corrosion Science, p. 731, 1997

(8) H. Tsuchiya, S. Fujimoto, O. Chihara and T. Shibata, Semiconductive Behavior of Passive Films Formed on Pure Cr and Fe-Cr Alloys in Sulfuric Acid Solution, Elec. Chem. Acta, p. 4357, 2002

(9) T. Shinohara, Application of Catalysis to Cathodic Protection of Metals, NIMS Report (draft)

(10) S. Fujimoto, T. Yamada and T. Shibata, Improvement of Pitting Corrosion Resistance of Type 304 Stainless Steel by Modification of Passive Film with Ultraviolet Light Irradiation, J. Electrochem. Soc., p. L79, 1998

Attachment (B). A Copy of Business Cards Collected

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