CONTAINER CORROSION WORKSHOP REPORT

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QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: None

ANALYSES AND CODES: None

1 CONTAINER CORROSION WORKSHOP SUMMARY

The corrosion workshop between the U.S. Nuclear Regulatory Commission (NRC) and the Center for Nuclear Waste Regulatory Analyses (CNWRA$^{®}$) was held on June 16, 2011, at CNWRA via audio connection with NRC. The workshop was conducted to support the NRC Integrated Spent Nuclear Fuel Regulatory Activities (ISFR) program, specifically on technical issues on engineered barriers. The workshop also provided an opportunity to disseminate information to NRC and CNWRA staffs to promote integration with other ISFR activities. The purpose of this report is to briefly summarize the topics addressed during the workshop. The meeting ended with a discussion of potential future technical activities relevant to container corrosion.

Attendees:

NRC:	Tae Ahn, Randy Fedors, Jack Gwo, Chris Markley, and Jim Rubenstone
CNWRA:	Florent Bocher (Division 18), Ken Chiang, Philippe Dubreuilh, Xihua He, Andy Jung, Todd Mintz, Roberto Pabalan, Osvaldo Pensado, David Pickett, Pavan Shukla, and Lietai Yang

The agenda for this workshop is in the appendix.

2 WASTE PACKAGE AND ENGINEERED BARRIER SYSTEM OVERVIEW IN SPENT FUEL/HIGH LEVEL WASTE DISPOSAL PROGRAMS (PHILIPPE DUBREUILH)

The waste package and engineered barrier systems are important components in spent fuel and high-level waste disposal programs in several countries. The main countries and the respective host rocks discussed are Sweden, Finland, and Canada in granite; Belgium, France, and Switzerland in clay; and Germany in rock salt. A typical design for granite host environments is an iron insert in a copper container, surrounded by a bentonite buffer. The unique Belgian design involves a concrete-filled “supercontainer.” Other designs utilize stainless steel or carbon steel outer containers emplaced horizontally or vertically.

3 GEOCHEMICAL ENVIRONMENT (ROBERTO PABALAN)

Waste container performance in geologic repositories for nuclear waste will depend on the geochemical environment surrounding the containers. The important physical and chemical parameters that could affect waste container corrosion are temperature and the quantity and chemistry of water contacting the waste container. The important chemical parameters are pH; redox potential (Eh) or O_2 concentration; and the concentration of inorganic species, such as chloride, carbonate, and sulfur species, as well as organic ligands. The gap between the container and adjacent engineered barrier system material or host rock could be important for crevice corrosion processes. Microbes also could affect waste container corrosion, but this subject is outside the scope of the present discussion of the geochemical environment.

The parameters listed in the preceding paragraph are functions of the repository environment and design, including the host rock type and buffer/backfill materials. For example, the initial mineralogy and water chemistry of the geochemical environment will be different for a bentonite buffer/backfill system compared to argillaceous, crystalline, and salt host rocks. Also, the chemical evolution of water contacting waste containers will be affected by interactions between the groundwater and host rock and between groundwater and EBS materials (including waste container, buffer/backfill, and cementitious materials). In addition, these parameters will change with time.

4 CANDIDATE CONTAINER MATERIALS IN VARIOUS COUNTRIES AND CORROSION BEHAVIOR

4.1 Copper (Andy Jung)

Copper is a corrosion allowance material considered as a candidate for waste container material (waste package or canister) in Sweden, Finland, Canada, Japan, and Korea, specifically in a reducing granite rock environment. In an initial warm and oxidizing environment, species such as dissolved oxygen and chloride in the groundwater will be major factors affecting the corrosion process of copper. In an oxygen-depleted reducing environment, copper is thermodynamically stable in contact with water. However, when sulfur is present in the groundwater, sulfur can oxidize copper to copper sulfide, causing corrosion of copper. Another potential mechanism of corrosion of copper under reducing conditions is water corrosion by protons in pure water under oxygen-free conditions. However, until now, there has been no solid evidence as to whether this process could occur for canisters {such as those that are 5 cm [2 in]} thick protected by bentonite. Other factors influencing long-term copper corrosion could include stress corrosion cracking (SCC) due to a combination of strain and aggressive near-field water chemistry, salt deposit corrosion, galvanic corrosion of copper when contacting an inner iron shell, and radiation effects due to radiolysis of gas and water. Among these, more detailed studies appear to be warranted on SCC, salt deposit corrosion, the effect of an iron inner shell on copper corrosion, and potentially high concentrations of sulfide.

4.2 Carbon Steel (Tae Ahn)

Carbon steel is a corrosion-allowance candidate material considered primarily in France and Japan under reducing disposal conditions. Pitting corrosion is observed in the initial oxidizing environment and merges with general corrosion as the general corrosion penetration proceeds and pitting corrosion rate decreases. Therefore, performance assessment model abstractions are primarily based on the low general corrosion rates under reducing conditions. An enhancement factor is also considered to capture the effects of initial oxidizing conditions and temperature variations. Other potential corrosion modes include SCC, hydrogen-induced cracking, microbially influenced corrosion, corrosion with salt deposits, and radiolysis effects. More detailed studies appear warranted on hydrogen-induced cracking and enhanced corrosion with salt deposits. Carbon steel corrosion in alkaline environments is expected in a concrete-reinforced disposal setting or in the rebar of the concrete overpack in extended storage areas.

4.3 Titanium (Xihua He)

Titanium is a candidate material in various countries for the waste container and engineered barrier material in geologic disposal systems and in a rock salt environment. Titanium is corrosion resistant because of its passive film. However, crevice corrosion may become the lifetime limiting factor for titanium that is not alloyed with noble elements. Alloys of titanium with palladium have shown to be resistant to pitting and crevice corrosion in a wide range of chemical environments, even in the rock salt environment in Germany. For titanium grades alloyed with noble elements, the main corrosion issues are fluoride attack and hydrogen-induced cracking. However, degradation mechanisms are site specific. Depending on the geologic disposal site, relevant degradation mechanisms need to be evaluated.

4.4 Stainless Steel (Xihua He)

Stainless steel is a candidate engineered barrier material, but it is not proposed to be the primary waste container material. Stainless steel is often used in conjunction with cementitious material to improve corrosion resistance. Stainless steel is susceptible to pitting, crevice corrosion, microbially influenced corrosion, and SCC in a wide range of chemical environments. Depending on the site, each degradation mechanism has a different risk that can compromise containment.

4.5 Stress Corrosion Cracking of Stainless Steel (Ken Chiang and Pavan Shukla)

316 stainless steel is a material that might be used to construct engineered barrier materials because of its corrosion resistance. One degradation mode for 316 stainless steel is SCC. SCC may occur when a susceptible material, environmental conditions, and stress are present simultaneously. SCC susceptibility of 316 stainless steel was assessed in three potential disposal environments: (i) rock salt, (ii) bentonite clay, and (iii) granite. Based on literature information on chemical and thermal conditions of potential disposal environments and literature data on SCC susceptibility of 316 stainless steel in different aqueous solutions, it is concluded that (i) 316 stainless steel appears susceptible to SCC in a potential rock salt disposal environment, (ii) 316 stainless steel is not susceptible to SCC in a potential bentonite clay disposal environment, and (iii) there is not enough information available to assess SCC susceptibility of the alloy in a potential granite disposal environment.

4.6 Stress Corrosion Cracking Estimate for Crack Opening Area (Tae Ahn and Jack Gwo)

Once SCC occurs, it is important to assess the opening surface area of the container surface that allows radionuclide release. An evaluation is made on existing models based on the applied stress for the opening surface area caused by SCC. The stress conditions determine crack distributions (i.e., size and number of cracks). The models are applied to various disposal containers under seismic and nominal conditions. Performance assessment models [e.g., Scoping Options for Analyzing Risk (SOAR)] are exercised to understand the sensitivities of radionuclide release to the opening surface area. Under seismic conditions, impact stress in a deformed area is considered, whereas weld residual stress in a weld area is considered under nominal conditions.

4.7 Estimating the Extent of Damage to Waste Package Surface by Localized Corrosion (Pavan Shukla)

In the SOAR model, important parameters are needed to compute the consequences of radionuclide release to the environment, including the failure time of packages enclosing waste forms and the extent of damage to the waste package surface. Radionuclide releases from the waste package are a function of the extent of damage, generally specified in the form of a surface fraction. The breach area fraction of the waste package surface is estimated using (i) literature information, (ii) a physico-chemical model, and (iii) a geometric model. The literature information is based upon published experimental results on pitting of stainless steel in various salt solutions. The literature information indicates that the pitting area (i.e., area of pit covering the metal) is no more than 1 percent of the total surface area. It also indicates that the breach area fraction cannot exceed more than 25 percent. This value of breach area fraction is based upon reasonable values of electrochemical conditions that could arise at the stainless steel waste package surface in the potential repository environments. Additional work would determine the range of electrochemical conditions that could arise in different disposal environments. Additional studies involving different analogs could help validate the modeling results.

5 ENVIRONMENTAL DEGRADATION OF CONTAINER MATERIALS IN ROCK SALT FORMATION AND DEEP BOREHOLE DISPOSAL

5.1 Geochemical Environment in Rock Salt Formation (Roberto Pabalan)

Salt rock formation properties considered favorable for nuclear waste disposal include low water content and the lack of a mechanism and pathway for aqueous transport of radionuclides. However, there is significant uncertainty on the hydrologic isolation of salt formations. Posey and Kyle (1988), who reviewed various studies that have been conducted to evaluate the assumed salt rock formation properties and the potential use of salt deposits for nuclear waste storage, concluded that some salt domes are not as stable and dry as originally assumed, especially under mining conditions. In addition, rock salt formations are not necessarily dry due to the presence of intragranular water in salt minerals, typically in the form of fluid inclusions or as waters of hydration in hydrous minerals. These waters may get mobilized in response to thermal gradients generated by the high-level waste and accumulate at the hot waste container surface. This process, in addition to water intrusion from overlying groundwater aquifers, may cause corrosive brines to contact and corrode the waste containers.

The chloride-rich brines from rock salt formations either are Na-Mg-K chloride brines or NaCl brines. There are very limited Eh data, but the few measurements indicate the brines are reducing. Because salt solubility generally increases with temperature, brine concentrations likely will increase with temperature. However, oxygen concentration decreases with increasing ionic strength, which could mitigate the effect of increased temperature on corrosion rate. Gases such as H_2S, HCl, CO_2, and SO_2 could be released from salt minerals upon heating, which in turn could change the pH of solutions contacting the waste container.

5.2 Container Material Degradation in Rock Salt Formation (Todd Mintz)

Factors affecting waste package degradation in a rock salt host include the chloride-containing solution and temperature. Temperature varies but may be as high as a couple of hundreds of degrees Celsius. Corrosion-resistant materials, such as titanium, nickel-based alloy, and stainless steel, and corrosion allowance materials, such as cast iron and steel, are the candidate materials for the container. The container with corrosion-resistant materials has the following features: (i) smaller and lighter, (ii) low general corrosion rates, (iii) larger susceptibility to localized attack, (iv) potential susceptibility to hydrogen embrittlement, and (v) possibly enhanced corrosion by radiation field.

In comparison, the corrosion allowance materials have the following features: (i) larger and heavier, (ii) larger general corrosion rates, (iii) lower susceptibility to localized attack, and (iv) possibly enhanced corrosion by radiation field.

5.3 Waste Package Options in Deep Borehole Design (Xihua He)

Deep borehole disposal is one of several options for permanent disposal of high-level waste and spent fuel. The process consists of drilling a borehole into crystalline basement rock, typically granite, to depths up to 5,000 m [1,640 ft]. Waste packages would be emplaced in the lower 2,000 m [6,562 ft] of the borehole. The upper 3,000 m [9,843 ft] would then be sealed. In this concept, the waste container may not be needed, because the surrounding media will hold the package in place. The materials proposed for containers include copper, titanium, lead, and steel.

6 DATABASE ON WASTE CONTAINER MATERIALS AND CORROSION ISSUES IN VARIOUS GEOLOGIC DISPOSAL SYSTEMS (FLORENT BOCHER)

A database was developed to store a large number of study results from various laboratories. The database is expected to be searchable using multiple filters, be remotely accessible, and be modular and adaptable. The variables identified are currently divided into three groups: (i) environment, (ii) structure, and (iii) study. Nearly 1,500 entries are currently in the database. Online access has been tested successfully. The database is not expected to be limited to European countries but also includes studies performed in Asia (Japan, South Korea) and historical studies performed in the United States. Discussion with the various types of users will be initiated to obtain user feedback. At this point in time, the current database is being shown as a proof of concept of capabilities. Additional involvement by database deployers of online solutions will be pursued. Examples of the successful application of a database to the scientific community can be found in the JAEA Nuclide Migration Database. However, such a database structure is currently outside the scope of this project.

7 STATUS OF INDEPENDENT CORROSION STUDIES OF ENGINEERED BARRIER MATERIALS

7.1 Background on Dripping and Humid Air Tests (Tae Ahn)

Current tests are based on the proposed Yucca Mountain repository environment, where aqueous conditions are dripping seepage groundwater. Future tests will be connected to alternative disposal settings. The test results of dripping groundwater and humid air could be used to understand corrosion under salt deposits, which can occur in various geological disposal settings with backfill.

7.2 Alloy 22 and 316L Stainless Steel Tests Under Dripping Condition (Andy Jung)

Corrosion tests of two alloys (i.e., Alloy 22 and 316L stainless steel) were conducted under seepage water dripping conditions at different temperatures and relative humidities. In all of the tested conditions for Alloy 22 and stainless steel, white deposits were observed on the posttest specimens. Removing the salts and corrosion products per ASTM G1-03 procedures, the surfaces of test samples exhibited several corrosion pits. However, there was no clear evidence of pit propagation with time. For the case of Alloy 22, the corrosion rate measured by the weight loss method decreased with time and was close to the rates obtained from immersion tests in the literature.

The main source of uncertainty of the corrosion rates is likely from the weight loss measurement of Alloy 22, requiring the use of a high precision microbalance. In addition, to increase measurement sensitivity of weight loss, the specific surface area of test samples was maximized by using a very thin metal sheet. Other sources of uncertainties could include slightly different initial conditions of test samples, possible local differences in temperature and humidity inside the chamber, slightly different locations of dripping water onto the sample surface and amount of salt deposited, surface area extent on the back side wetted with dripped water, possible effects of the mechanical impingement of the water droplet, and the dynamic process of dripping water volume. Additionally, a relatively small number of test samples may also limit the statistical confidence of the corrosion rate data.

7.3 Titanium Corrosion Test Under Dripping Condition (Xihua He)

Some titanium corrosion rates from dripping are similar to those reported in the literature under immersion conditions. Longer term tests under dripping are planned to understand the high corrosion rates, and other tests or modeling under disposal system alternatives, such as a rock salt environment may be considered. In the dripping test, Teflon is used in the chamber. We may need to consider possible outgassing of fluoride from Teflon and its effect on titanium corrosion. A fluoride-sensitive electrode may be used in the test to monitor fluoride.

7.4 Borated Stainless Steel in Humid Air (Xihua He)

Corrosion rates for borated stainless steel in humid air are lower than those reported in the literature; however, pitting corrosion was observed from tests at 75 and 90 °C [167 and 194 °F]. Longer tests and tests in other solutions are ongoing. For these ongoing tests, boron location and concentration will be analyzed to understand boron dissolution from the material at the end of tests. Future tests may consider spent fuel pool water in connection with the application in extended storage.

8 REFERENCE

Posey, H.H. and J.R. Kyle. “Fluid-Rock Interactions in the Salt Dome Environment: An Introduction and Review.” *Chemical Geology*. Vol. 74. pp. 1–24. 1988.

APPENDIX

INTEGRATED SPENT FUEL REGULATORY ACTIVITIES CORROSION WORKSHOP AGENDA

Appendix—Integrated Spent Fuel Regulatory Activities Corrosion Workshop Agenda

Thursday, June 16, 2011, 8:30 a.m.—3:00 p.m. central daylight time; NRC–CNWRA
(Room 237, Bldg. 189)

8:30 a.m. Waste package and engineered barrier system overview in spent fuel/high-level waste disposal programs (Philippe Dubreuilh)
Geochemical environment (Roberto Pabalan)

9:15 a.m. Proposed container materials and their corrosion behavior

- Copper (Andy Jung)
- Carbon steel (Tae Ahn)
- Titanium (Xihua He)
- Stainless steel (Xihua He)
- Stress corrosion cracking of stainless steel (Ken Chiang, Pavan Shukla)
- Stress corrosion cracking estimate for crack opening area (Tae Ahn, Jack Gwo)
- Estimating the extent of damage to waste package surface by localized corrosion (Pavan Shukla)

11:35 a.m. Lunch break

12:45 p.m. Environmental degradation of container materials in rock salt formation and deep borehole disposal

- Geochemical environment in rock salt formation (Roberto Pabalan)
- Container material degradation in rock salt formation (Todd Mintz)
- Waste package options in deep borehole design (Xihua He)

1:35 p.m. Database on waste container materials and corrosion issues in various geologic disposal systems (Florent Bocher)

2:05 p.m. Status of independent corrosion studies of engineered barrier materials

- Background on dripping and humid tests (Tae Ahn)
- Alloy 22 and 316L stainless steel (Andy Jung)
- Titanium (Xihua He)
- Borated stainless steel in humid air (Xihua He)

2:35 p.m. Thoughts on SOAR related to container corrosion (All)

2:50 p.m. Staff discussion on potential tasks considering NRC priorities

3:00 p.m. Adjourn